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ATMOSPHERIC DEPOSITION ON SWISS LONG-TERM FOREST ECOSYSTEM RESEARCH (LWF) PLOTS

ANNE THIMONIER[1], MARIA SCHMITT[1,*], PETER WALDNER[1], and BEAT RIHM[2]
[1]*WSL - Swiss Federal Institute for Forest, Snow and Landscape Research, Zürcherstrasse, Birmensdorf, Switzerland;* [2]*Meteotest, Fabrikstrasse, Bern, Switzerland*
*(*author for correspondence, e-mail: maria.schmitt@wsl.ch)*

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Abstract. Atmospheric deposition of the major elements was estimated from throughfall and bulk deposition measurements on 13 plots of the Swiss Long-Term Forest Ecosystem Research (LWF) between 1995 and 2001. Independent estimates of the wet and dry deposition of nitrogen (N) and sulfur (S) on these same plots were gained from combined simplified models. The highest deposition fluxes were measured at Novaggio (Southern Switzerland), exposed to heavy air pollution originating from the Po Plain, with throughfall fluxes averaging 29 kg ha^{-1} a^{-1} for N and 15 kg ha^{-1} a^{-1} for S. Low deposition fluxes were measured on the plots above 1800 m, with throughfall fluxes lower than 4.5 kg ha^{-1} a^{-1} for N and lower than 3 kg ha^{-1} a^{-1} for S. The wet deposition of N and S derived from bulk deposition was close to the modeled wet deposition, but the dry deposition derived from throughfall was significantly lower than the modeled dry deposition for both compounds. However, both the throughfall method and the model yielded total deposition estimates of N which exceeded the critical loads calculated on the basis of long-term mass balance considerations. These estimates were within or above the range of empirical critical loads except above 1800 m.

Keywords: atmospheric deposition, critical load for nitrogen, long-term forest plot, modeling, risk assessment, throughfall

1. Introduction

The release of pollutants into the atmosphere increased massively during the last century, raising serious concerns about the effects of atmospheric deposition on forest ecosystems in Central Europe and elsewhere. In Switzerland, emissions of air pollutants such as sulfur dioxide and oxidized nitrogen compounds have been substantially reduced in the last 15 years, with the implementation of various measures targeting a pre-1950 level (BUWAL, 1995). However, whereas sulfur emissions are expected to stabilize below the 1950 level, nitrogen emissions still exceed this level. In general, the main nitrogen sources are emissions of nitrogen oxides from combustion processes and emissions of ammonia from agricultural activities. In Switzerland, motor transport, which makes up 70% of combustion processes, released 25.0 kt NO_x-N out of a total of 41.4 kt NO_x-N for 1995. Agricultural activities released 45.4 kt NH_3-N out of a total of 49.6 kt (BUWAL, 1995).

Nitrogen can act as a fertilizer and enhance forest growth (Spiecker, 1999). However, elevated nitrogen inputs represent a potential threat to the stability of forest ecosystems: enhanced nitrogen deposition can lead to nutrient imbalances, soil acidification, changes in the composition of the ground vegetation, changes in mycorrhizae, and increased susceptibility to secondary stresses (Skeffington and Wilson, 1988). "Nitrogen saturation" may be reached when the availability of inorganic nitrogen is in excess of the plant and microbial nutritional demand and the ecosystem is unable to retain all the incoming nitrogen (Aber *et al*., 1989), leading to increased nitrogen leaching below the rooting zone. The sensitivity of forest ecosystems to nitrogen deposition in the long term has been formalized using the concept of "critical loads", defined as a quantitative estimate of an exposure to a nitrogen deposition below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge (Nilsson and Grennfelt, 1988).

Two approaches can be used to quantify atmospheric deposition on a given location: (i) measurements on the site itself, or (ii) application to the site of a model calibrated for the region of interest using available datasets, surveys and field information.

In Switzerland, the first approach (measurements) has been used since the mid-1980s to quantify wet and dry deposition at a few forest sites in projects which were often motivated by a growing concern over the effects of air pollution on forest health (e.g. Flückiger *et al*., 1986; Kloeti *et al*., 1989; Haemmerli *et al*., 1992; Flückiger and Braun, 1998; Schleppi *et al*., 1998). In the mid-1990s, a network of 17 selected forest sites was set up within the framework of the Swiss Long-Term Forest Ecosystem Research (LWF, according to the German: Langfristige Waldökosystem-Forschung) to improve our understanding of how natural and anthropogenic stresses affect forests in the long term (Cherubini and Innes, 2000; Thimonier *et al*., 2001). LWF meets the aims of the International Co-operative Programme on the Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests), which was implemented under the Convention on Long-range Transboundary Air Pollution of the UN/ECE (EC-UN/ECE *et al*., 2001).

On selected LWF plots, atmospheric deposition is assessed with the throughfall method (Draaijers *et al*., 1996). This method relies on the parallel sampling of precipitation under the forest canopy (throughfall) and precipitation in a nearby open area. Throughfall reflects the composition of both incident precipitation (wet deposition) and dry deposition, as the substances deposited during dry periods on branches and foliage are partly washed out during subsequent precipitation. Wet deposition is obtained directly from sampling in the open field if "wet-only" collectors (which are open only when it rains) are used. If continuously open collectors are used (bulk precipitation), correction is needed for deposition of particulate material on the collectors during dry periods. Dry deposition on forests is considerably higher than dry deposition in the open field due to the roughness of the canopy, the large surface areas developed by the foliage and the physical

and physiological properties of the leaves (cuticular adsorption, stomatal uptake of gases). Estimates of dry deposition on forests can be derived from the difference between throughfall and wet or bulk precipitation, so long as a number of assumptions about the canopy exchange processes (uptake and leaching of nutrients) are made.

The second approach to quantifying nitrogen deposition (modeling) involves first calculating concentrations in the atmosphere. This can be done either by using emission inventories and chemical transformations of each emitted component in simulating atmospheric dispersion (transport model), or by extrapolating point measurements using known geographical parameters such as land use, topography or road networks (geo-statistical methods). The wet deposition is then obtained by multiplying the concentrations in precipitation with the precipitation amounts, and the dry deposition by multiplying air concentrations with deposition velocities (inferential modeling). These deposition velocities depend on the reactivity of the compound, land use, vegetation type and, for some models, on additional factors such as boundary layer turbulence. The deposition of sulfur and nitrogen across Europe has been calculated with this approach at a spatial resolution of 50 km $\times$ 50 km and a high temporal resolution (EMEP, see e.g. Jonson *et al.*, 1998). The approach was adapted in the mid-1990s by Rihm (1996) so that the regional distribution of nitrogen deposition in Switzerland could be calculated at a higher spatial resolution (1 km $\times$ 1 km).

In this paper we present the results of throughfall sampling on 13 LWF sites, for which up to 7 years of measurements are available. We also analyze the output of the deposition model developed by Rihm (1996), which was run for these 13 sites to calculate recent annual wet and dry deposition of nitrogen and sulfur. We address then three main questions: (1) How well does the atmospheric deposition derived from throughfall measurements compare with the modeled nitrogen and sulfur deposition? (2) Where do the inconsistencies, if any, come from? (3) On which LWF plots does nitrogen deposition exceed the critical load and thus represent a potential risk for the forest ecosystem?

2. Methods

2.1. Study sites

Throughfall chemistry was monitored on the 13 LWF plots selected for at least one year. Precipitation was sampled in parallel using continuously open collectors (bulk precipitation) in open areas close to the forest plots. The collectors in the open area were next to a meteorological station also run by LWF that recorded precipitation with a tipping bucket, air temperature, humidity, solar radiation, UV-B and PAR radiation, and wind speed and direction. The study sites are located in various regions of Switzerland. Two plots (Bettlachstock (BET),

Figure 1. Location of LWF plots (results for the plot in Visp are not given as sampling only started in 2001) (Swiss Federal Statistical Office/Federal Office of Topography).

Neunkirch (NEU)) are located in the Jura mountains; four (Jussy (JUS), Lausanne (LAU), Othmarsingen (OTH), Vordemwald (VOR)) on the Central Plateau; three (Alptal (ALP), Beatenberg (BEA), Schänis (SCH)) in the Lower Alps; two (Celerina (CEL), National Park (NAT)) in the Alps; and two (Chironico (CHI), Novaggio (NOV)) in the Southern Alps (Figure 1). The site characteristics are shown in Table I.

2.2. Sampling design in the field

Throughfall collectors were divided into two sets of equal numbers, and systematically distributed in two 43 m × 43 m subplots inside the forest plot. One of each pair of subplots is dedicated to the intensive monitoring of soil chemistry (solid phase and soil solution), litterfall and ground vegetation in addition to throughfall. The other subplot, which is adjacent to the intensive monitoring subplot in most cases, was designed to cover the spatial variability of the forest stand better. Collectors of the same design were used in the forest stands and the open area, but the type and number of collectors installed varied depending on the amount of snowfall expected during winter.

(a) Sampling design when no significant snowfall was expected (funnel type collectors): Funnel-type collectors were used throughout the year on plots where snow precipitation is not expected to be abundant in winter (NEU; JUS, LAU,

TABLE I

Site description. Jussy is divided in two subplots, one unmanaged, one managed. Long-term mean annual precipitation amounts were derived from precipitation maps established for the period 1972–1992 (FOWG, 2000)

Region	Site		Longitude	Latitude	Altitude a.s.l. (m)	Main tree species	Age of the main tree species (yr)	Mean precipitation (mm)	Sampling years
Jura	BET	Bettlachstock	07°25	47°14	1149	*Fagus sylvatica*	170	1549	1999–2001
	NEU	Neunkirch	08°32	47°41	582	*Fagus sylvatica*	150	1044	1998
Central Plateau	JUS	Jussy	06°17	46°14	501	*Quercus robur*	80	977	1998–2001
	LAU	Lausanne	06°40	46°35	807	*Fagus sylvatica*	150–160	1210	1997–2001
	OTH	Othmarsingen	08°14	47°24	484	*Fagus sylvatica*	110–130	1123	1995–2001
	VOR	Vordemwald	07°53	47°17	480	*Abies alba*	100	1115	1997–2001
Lower Alps	ALP	Alptal	08°43	47°03	1160	*Picea abies*	170–220	2286	1997–1998
	BEA	Beatenberg	07°46	46°43	1511	*Picea abies*	180–220	1305	2000–2001
	SCH	Schänis	09°04	47°10	733	*Fagus sylvatica*	120–140	1801	1999–2001
Alps	CEL	Celerina	09°53	46°30	1871	*Pinus cembra*	200–240	1024	1999–2001
	NAT	National Park	10°14	46°40	1899	*Pinus mugo*	200	1048	1999–2001
Southern Alps	CHI	Chironico	08°49	46°27	1365	*Picea abies*	150–170	2187	2001
	NOV	Novaggio	08°50	46°01	950	*Quercus cerris*	60	2017	1997–2001

OTH, VOR) and only during the snow-free season on plots where heavy snowfall is likely in winter (BET; ALP, BEA, SCH; CEL, NAT; CHI, NOV) (Figure 1).

The funnel-type collectors consisted of a funnel with a 100 cm^2 opening, connected to a 2 l storage bottle (see also description in Thimonier (1998a, 1998b)). The collectors were installed in PVC-pipes in order to shield the samples from direct solar radiation, and were equipped with guard rings to reduce the risk of contamination by bird droppings. Contamination with organic material was minimized by using two filters. The first was a polyethylene disk (diameter 55 mm) placed inside the funnel to prevent contamination with coarse material and the second a polyester net fitted between the funnel and the storage bottle to avoid contamination with fine material. Initially, this net consisted of a piece of fabric with a mesh size of 30 μm. From March 2001 onwards, however, we used a net with a larger mesh size (250 μm) and a tighter connection between the funnel and the storage bottle to prevent water running on the outer wall flowing into the bottle through this net (Draaijers *et al.*, 2001).

Bulk precipitation was sampled with three collectors in the open area. The opening of the collector was set at a height of 1.5 m above ground. In the forest stand, throughfall was sampled either with 16 collectors or, at CHI, with 8 collectors at a height of 1 m and distributed over the two 43 m $\times$ 43 m subplots. At OTH, where throughfall sampling began before the sampling design was standardized for all plots, the collectors were originally located in lines (Thimonier, 1998b). The intensive monitoring subplot on which eight collectors were subsequently relocated was installed in 1998. We kept only the eight collectors which were in use throughout the whole 1995–2001 period for our calculations.

Precipitation samples were collected every two weeks and either directly brought back to the laboratory or sent by post in insulated boxes. On each sampling occasion, the whole collector (funnel, filters and storage bottle) was replaced by a clean one that had been acid washed or rinsed with deionized water in the laboratory.

(b) Sampling design when abundant snowfall was expected (bucket-type collectors or plastic bags): Snow collectors were used in winter on plots where snow precipitation is expected to be abundant. Two types of collectors were used: 30-cm diameter buckets equipped with plastic bags before and after the winter period 1998–1999 and long plastic bags fitted to a 20 cm diameter PVC ring during the winter 1998–1999. This second type of snow collector with a smaller surface area was selected to reduce the frequency of the bucket collectors overflowing, which occurred on a number of occasions during the previous winter. However, the smaller areas made the collecting less efficient as, under certain conditions, a snowcap formed, so buckets were used again in the following winters.

Access to the plots is difficult in winter, as the roads are often closed due to snow, so that it is necessary to walk further carrying a lot of equipment and samples with greater risks of avalanche danger. Hence, the number of collectors was significantly reduced in winter, with only one collector in the open area, and four in the forest

stand (except at CHI where no snow sampling was performed in the stand). The four snow collectors in the forest stand were distributed on the two 43 m × 43 m subplots and each was placed close to a funnel-type collector location.

Precipitation samples were collected every two weeks, except at BET and CEL where the collection interval was extended to four weeks for logistic reasons. A new plastic bag was installed in the buckets (or the PVC rings). When sampling was carried out by the WSL staff, the whole sample was taken back to the laboratory. When sampling was carried out by a local forester, the amount of precipitation was determined with a spring balance and a subsample of the melted sample was sent by post in insulated boxes to the laboratory. On a few occasions when the collectors were filled with snow and access to the plot was particularly difficult, all four collectors were weighed but only a subset was carried back for chemical analyses. The remaining collectors were emptied in the field.

2.3. Sample preparation and chemical analyses

The time between sample collection and sample preparation was generally shorter than 3 days, and sometimes samples could be prepared within a day. All samples were either prepared immediately upon arrival or stored at 2 °C. During its preparation, each sample was weighed and its conductivity measured (reference temperature 20 °C). If bird droppings in the funnels or the buckets were reported on the field form, the sample was discarded. In addition, conductivity was used to detect possible contamination of the bulk precipitation samples. The spatial variability of atmospheric deposition should be rather low in open areas. Under this assumption, where funnel-type collectors were used, one of the three samples was discarded if it showed a conductivity that exceeded the average of the conductivities of the other two by more than 2 μS cm^{-1} and by more than 10%. The remaining samples were then merged, resulting in composite samples of either bulk precipitation or throughfall.

For each sample its pH was measured and it was then filtered (0.45 μm) and prepared in duplicate, one for chemical analysis, the other for storage at either −20 °C (samples for analyzing ammonium) or +2 °C (other samples) until validation of the analyses. Ammonium (NH_4^+) was determined colorimetrically with automated flow injection analysis (FIA). Calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and total phosphorus (P) were determined on acidified samples (1.13% HNO_3-Suprapur) with inductively coupled plasma-mass spectrometry (ICP-MS). From March 2000 onwards, these elements were determined with inductively coupled plasma-atomic emission spectrometry (ICP-AES). Nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-) were identified using ion chromatography (IC). The total dissolved nitrogen (TDN) was measured with alkaline persulfate oxidation (converting all nitrogen into nitrate) until the beginning of 2001. After March 2001, TDN was analyzed using a TOC-V analyser (Shimadzu, Tokyo, Japan) after acidification to

pH 2–3 with combustion at 720 °C (converting all nitrogen to nitrogen monoxide) and chemiluminescence gas detection. Our quality controls showed that the alkaline persulfate oxidation method led to irregular contaminations of the samples and the TOC-V analyser seemed to underestimate TDN. Therefore fluxes of dissolved organic nitrogen (DON = TDN−NH_4^+−N−NO_3^-−N) were only calculated approximately and were not included in the atmospheric deposition estimates, as discussed later in this paper. All the analyses were checked against certified standards and the WSL laboratories regularly participate in international comparison exercises (e.g. Mosello *et al*., 1998). Checking of the analytical results was based on the ion balance and comparing the measured and calculated conductivity (Rossum, 1975; Mosello *et al*., 1998). Duplicates of questionable samples were re-analyzed.

2.4. Estimating missing precipitation amounts and concentrations

For 2.7% of all collection intervals the precipitation exceeded the storage capacity of the collectors and the precipitation amount had to be estimated. We used regressions of precipitation amounts measured by our collectors against the precipitation data from the tipping bucket installed in the open area and on the forest plots, or against the data of the closest stations of the Swiss Meteorological Institute (MeteoSwiss). Missing element concentrations on a given plot were similarly estimated using regressions between parameters or between concentrations in bulk and throughfall samples observed for that plot.

At CHI, where throughfall was measured during summer only, the amount of winter throughfall was estimated from the winter bulk precipitation using a linear regression of the amount of summer throughfall against the summer bulk precipitation. The N and S concentrations of the winter throughfall were set to the volume-weighted means of N and S concentrations in the summer throughfall. A test of this approach with the data of a comparable plot, BEA, resulted in relative differences between reconstructed and measured annual fluxes of −4.4% for inorganic N and +4.9% for S on average over 3 years of measurements.

2.5. Estimation of atmospheric deposition from throughfall measurements

Throughfall (TF) and bulk precipitation (BP) fluxes were calculated multiplying precipitation amount and concentrations for each collection interval and were summed over calendar years, using interpolations at transitions between years. To estimate the wet (WD) and dry (DD) components of the total atmospheric deposition on the forest (TD) from TF and BP, several corrections have to be made.

To estimate WD, BP must be corrected for dry deposition onto the funnels. We applied average wet-only to bulk ratios (f_{corr}) given in the literature (Draaijers *et al*.,

1998) to our annual fluxes of bulk precipitation.

$$\mathrm{WD} = \mathrm{BP} \cdot f_{\mathrm{corr}} \tag{1}$$

To estimate TD, we used the canopy budget model developed by Ulrich (1983), extended by Draaijers and Erisman (1995) and synthesized in EC-UN/ECE *et al.* (2001). In this model throughfall fluxes represent TD plus or minus canopy exchanges (CE), which are the result of canopy leaching (Cle) and canopy uptake (CU).

$$\mathrm{TF} = \mathrm{TD} \pm \mathrm{CE} = \mathrm{TD} + \mathrm{Cle} - \mathrm{CU} \tag{2}$$

For sodium (Na^+), chloride (Cl^-) and sulfate (SO_4^{2-}), canopy exchange CE is negligible (e.g. Lindberg and Lovett, 1992) and TD is calculated as:

$$\mathrm{TD} = \mathrm{TF} \tag{3}$$

To estimate the total deposition of base cations, Na^+ is taken as a tracer having a TD/BP ratio similar to TD/BP for Ca^{2+}, Mg^{2+} and K^+ (particles containing Ca^{2+}, Mg^{2+} and K^+ are assumed to have the same mass median diameter as Na^+ containing particles):

$$\mathrm{TD_{bc}} = \mathrm{TF_{Na}}/\mathrm{BP_{Na}} \cdot \mathrm{BP_{bc}} \tag{4}$$

where bc stands for Ca^{2+}, Mg^{2+} or K^+.

Canopy leaching of these cations (Cle_{bc}) is calculated as:

$$\mathrm{Cle_{bc}} = \mathrm{TF_{bc}} - \mathrm{TD_{bc}} \tag{5}$$

We calculated Equations (1)–(5) on an annual basis. This approach was successfully tested against the method using micrometeorological measurements and inferential modeling (Draaijers and Erisman, 1995).

For nitrogen compounds, estimating atmospheric deposition using throughfall data is more uncertain than for other elements. Several studies showed that nitrogen in gas form (NO_2, HNO_3, NH_3) or in solution (NH_4^+, NO_3^-) can be taken up by foliage (see review by Harrison *et al.*, 2000). In the extended canopy budget model (EC-UN/ECE *et al.*, 2001), canopy uptake (CU) of NH_4^+ and H^+ is assumed to be equal to the total canopy leaching of Ca^{2+}, Mg^{2+} and K^+ taking place through ion exchange, corrected for the leaching of weak acids (wa).

$$\mathrm{CU_{NH_4}} = (\mathrm{Cle_{Ca}} + \mathrm{Cle_{Mg}} + \mathrm{Cle_K}) - \mathrm{Cle_{wa}} - \mathrm{CU_H} \tag{6}$$

with

$$\mathrm{CU_H} = 6 \cdot \mathrm{TF_H}/(\mathrm{TF_{NH4}} + 6 \cdot \mathrm{TF_H}) \cdot (\mathrm{Cle_{Ca}} + \mathrm{Cle_{Mg}} + \mathrm{Cle_K} - \mathrm{Cle_{wa}}) \tag{7}$$

and

$$\mathrm{Cle_{wa}} = \mathrm{TF_{wa}} - 2 \cdot \mathrm{BP_{wa}} \tag{8}$$

where wa was calculated as the difference in equivalent concentration of cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, NH_4^+) minus strong acid anions (SO_4^{2-}, NO_3^-, Cl^-).

Assuming that NH_4^+ has an exchange efficiency six times larger than NO_3^-, canopy uptake of N is calculated as (in equivalent):

$$\mathrm{CU_N} = \mathrm{CU_{NH4}} \cdot (\mathrm{TF_{NH4}} \cdot 6 + \mathrm{TF_{NO3}})/(\mathrm{TF_{NH4}} \cdot 6) \tag{9}$$

Total deposition of nitrogen is then calculated as:

$$\mathrm{TD_N} = \mathrm{TF_N} + \mathrm{CU_N} \tag{10}$$

Dry deposition of all compounds is calculated as:

$$\mathrm{DD} = \mathrm{TD} - \mathrm{WD} \tag{11}$$

2.6. Modeled deposition of nitrogen and sulfur

Sulfur and nitrogen deposition on the LWF plots was calculated using the combined simplified model described by Rihm (1996), Kurz *et al*. (1998) and Rihm and Kurz (2001). Recent monitoring results for Southern Switzerland (Barbieri and Pozzi, 2001) and from a new NH_3-monitoring program carried out at 40 stations (Thöni *et al*., in press) have been included into the model, together with an update of the SO_2-concentration map. The model calculating N deposition at the 1 km × 1 km spatial resolution in Switzerland was parameterized so that the total nitrogen deposition in Switzerland calculated with this model approximately matched the deposition calculated by EMEP with a resolution of 50 km × 50 km (77.4 kt N a^{-1} in 1998, corresponding to 19 kg N ha^{-1} a^{-1} on average (EMEP, 2000)). The following compounds were considered in the calculation of N deposition: NO_3^- and NH_4^+ for wet deposition, and nitric acid vapor (HNO_3), the gases nitrogen dioxide (NO_2) and ammonia (NH_3), and particulate NH_4^+ and NO_3^- (aerosols) for dry deposition (Equation (12)). The calculation of S deposition included the calculation of the wet deposition of SO_4^{2-} and the dry deposition of sulfur dioxide (SO_2) (Equation (13)). Dry deposition of particulate SO_4^{2-}, which amounts to only a small fraction of the wet deposition (Hertz and Bucher, 1990), was not calculated.

$$\begin{aligned}\mathrm{TD_N} = {} & \mathrm{WD_{NH_4}} + \mathrm{WD_{NO_3}} + \mathrm{DD_{NH_3}} + \mathrm{DD_{NO_2}} + \mathrm{DD_{HNO_3}} \\ & + \mathrm{DD_{NH_4}} + \mathrm{DD_{NO_3}}\end{aligned} \tag{12}$$

$$\mathrm{TD_S} = \mathrm{WD_{SO_4}} + \mathrm{DD_{SO_2}} \tag{13}$$

(a) Wet deposition: Wet deposition was obtained by multiplying the mean annual concentrations of N and S compounds in precipitation with precipitation amounts from the mean annual precipitation map established by the Federal Office for Water and Geology (Table I). This map is based on about 300 precipitation measurement stations (FOWG, 2000). SO_4^{2-}, NO_3^- and NH_4^+ concentrations were set to values derived from 12 monitoring stations and stratified according to altitude. Mean annual concentrations of SO_4^{2-} in precipitation were considered to be homogenous below 1000 m and to decrease linearly with altitude above this limit (Table II). For NO_3^- and NH_4^+, a distinction was made between two regions. North of the Alps, the mean annual concentrations of N compounds in precipitation were, similar to SO_4^{2-}, considered to be homogenous below 1000 m and to decrease linearly with altitude above this limit. Due to the topography of the south face of the Alps, where the mountain chain acts as a specific barrier to the southern air mass transport, NO_3^- and NH_4^+ concentrations in precipitation were calculated as a function of altitude, longitude and latitude, according to the regression model of Barbieri and Pozzi (2001) also described by Barbieri *et al.* (2004).

(b) Dry deposition: Dry deposition of aerosols and gases was calculated by multiplying modeled air concentrations (annual means) with deposition velocities for forests taken from the literature (Rihm, 1994, 1996). For particulate NO_3^- and NH_4^+, concentrations (derived from a few point measurements) and deposition velocities were stratified according to altitude. In each class of altitudes, concentrations and deposition velocities were calculated by linear interpolation of the lower and upper limits of three altitude ranges (Table II). For HNO_3, concentrations were similarly stratified according to altitudes but the deposition velocity was set to a constant. NH_3 and NO_2 concentrations were derived from concentration fields calculated from emission inventories to which statistical dispersion models were then applied (SAEFL, 2004; Thöni *et al.*, 2004). The deposition velocities for NO_2 and NH_3 were set to values depending on the type of stand (coniferous or broadleaved). In Rihm (1996), the distinction between coniferous and broadleaved stands was not made in the calculations for NH_3. At that time, the deposition velocity was set to a single value (30 mm s^{-1}). SO_2 concentrations were mapped by geo-statistical interpolation of 52 stations and the deposition velocity was independent of the forest type.

The years of reference for SO_4^{2-} concentrations in precipitation were 1997–1999. For concentrations of N compounds in precipitation, the years of reference were 2000 north of the Alps, and 1993–1998 south of the Alps (Barbieri and Pozzi, 2001). The mean precipitation amounts were based on long-term precipitation data (1972–1992). For air concentrations, the year of reference was 2000 for all nitrogen compounds and SO_2.

TABLE II

Calculation of wet deposition (a) and dry deposition (b) of N and S on LWF plots with the modeling approach

(a) Concentrations of N and S in precipitation (wet deposition)

		Concentration (μeq l^{-1})	
Compound	Altitude range (m)	North of the Alps	South of the Alps
NH_4	≤1000	32.1	Function of altitude, longitude,
	2000	24.3	latitude (Barbieri & Pozzi, 2001)
NO_3	≤1000	23.6	Function of altitude, longitude,
	2000	17.9	latitude (Barbieri & Pozzi, 2001)
SO_4	≤1000	22.0	
	2000	17.5	

(b) Air concentrations of N and S and deposition velocities (dry deposition)

			Deposition velocity (mm s^{-1})	
Compound	Altitude range (m)	Concentration (μg m^{-3})	Coniferous forests	Broadleaved forests
Aerosols				
NH_4	400	2.02	2	2
	800	1.69	4	4
	2000	0.43	4	4
NO_3	400	2.79	2	2
	800	2.36	4	4
	2000	0.56	4	4
SO_4		Not calculated		
HNO_3	200	1		
	1000	0.5	15	15
	2000	0.25		
Gases				
NO_2	Emission inventory and dispersion model		4	3
NH_3	Emission inventory and dispersion model		30	22
SO_2	Geo-statistical interpolation		8	8

2.7. CRITICAL LOADS FOR NITROGEN

We compared the deposition data derived from our throughfall measurements and the modeled data with the critical loads for nitrogen (CL_N). The values of these critical loads were derived using two approaches: (1) the steady state mass balance

method (SMB), based on the nitrogen saturation concept (the nitrogen deposition must not lead to a situation where the availability of inorganic nitrogen is in excess of the total combined plant and microbial nutritional demand) (UBA, 1996; cited in Rihm, 1996, and Rihm and Kurz, 2001); and (2) the empirical method, based on data obtained from controlled chamber and field experiments, chemical analyses, comparisons of vegetation composition in time and space, ecosystem models and biological knowledge (Grennfelt and Thörnelöf, 1992; Rihm, 1996; Rihm and Kurz, 2001).

The SMB method uses the following equation (in Rihm, 1996):

$$\mathrm{CL_N} = U_\mathrm{N} + I_\mathrm{N} + \mathrm{le(acc)_N}/(1 - \mathrm{fde}) \tag{14}$$

where U_N is the amount of N removed by wood harvesting, I_N the acceptable immobilization rate of N in soil organic matter, $\mathrm{le(acc)_N}$ the acceptable total leaching from the rooting zone, and fde the denitrification fraction.

The removal by wood harvesting, U_N, was calculated by multiplying the N content of the stems with the long-term harvesting rate. The N content of stems was calculated using a wood density of 500 kg $\mathrm{m^{-3}}$ and a N content of 0.10% for coniferous forests (VOR; ALP, BEA; CEL, NAT; CHI), a wood density of 700 kg $\mathrm{m^{-3}}$ and a N content of 0.15% for deciduous forests (BET, NEU; JUS, LAU, OTH; SCH; NOV). For the long-term wood harvesting rates, the means for the five regions of Switzerland was taken (Central Plateau: 6.8 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for the deciduous forests (JUS, LAU, OTH), 8.5 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for the coniferous forests (VOR); Lower Alps: 4.1 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for the deciduous forests (SCH), 4.3 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for the coniferous forests (ALP, BEA); Alps: 2.9 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for coniferous forests (CEL); Southern Alps: 1.6 $\mathrm{m^3\ ha^{-1}\ a^{-1}}$ for coniferous forests (CHI)). For unmanaged plots U_N was set to 0.

The immobilization rate, I_N, was set to 3 kg N $\mathrm{ha^{-1}\ a^{-1}}$ at low altitudes (<500 m), 5 kg N $\mathrm{ha^{-1}\ a^{-1}}$ at high altitudes (>1500 m), and calculated by linear interpolation at altitudes in-between.

The acceptable total leaching, $\mathrm{le(acc)_N}$, was set to 4 kg N $\mathrm{ha^{-1}\ a^{-1}}$ for forests in the lowlands below 500 m (OTH, VOR) and 2 kg N $\mathrm{ha^{-1}\ a^{-1}}$ for alpine forests above 2000 m. It was calculated by linear interpolation at altitudes between 500 and 2000 m (all plots except OTH, VOR). These values have been changed compared to Rihm (1996), where $\mathrm{le(acc)_N}$ was set to 4 kg N $\mathrm{ha^{-1}\ a^{-1}}$ for coniferous forests and 5 kg N $\mathrm{ha^{-1}\ a^{-1}}$ for deciduous forests.

A value for fde was ascribed to each plot according to the degree of hydromorphy derived from the 1:200,000 soil suitability map of Switzerland (Bodeneignungskarte der Schweiz 1:200,000, 1980), as done by Rihm (1996). Lower values of fde were ascribed to dry soils, and higher values to wet soils.

Empirical critical loads were attributed to each plot according to the forest type (UBA, 1996): 7–20 kg N $\mathrm{ha^{-1}\ a^{-1}}$ for acidic coniferous forest (VOR, BEA,

CEL, CHI), 10–20 for acidic deciduous forests (JUS, LAU, OTH; SCH; NOV), and 15–20 for calcareous forests (BET, NEU; ALP; NAT).

3. Results

3.1. Precipitation and canopy interception

Annual precipitation varied markedly from site to site (Table III). The wettest sites were SCH, ALP (Lower Alps) and NOV (Southern Alps) with precipitation amounts in the open often exceeding 2000 mm. The lowest annual precipitations were recorded in NEU (Jura), CEL, NAT (Alps) and JUS (Plateau). Precipitation amounts varied considerably between the sampling years. NOV had the largest difference between years, with the precipitation recorded in 2000, the wettest sampling year (2771 mm in the open area) 68% higher than that measured in 1997, the driest year (1654 mm).

The relative rainfall interception was highest at OTH, JUS (broadleaved stands) and VOR (mixed stand), and lowest at ALP, NAT, CEL and CHI (coniferous stands), which are located at moderate and high elevations. The inter-annual variability of interception was high, probably due to the variable intensity and form (snow or rain) of the single precipitation events, which contribute to the overall pattern.

3.2. Concentrations

Concentrations in bulk precipitation were on average dominated by NO_3^-, NH_4^+, SO_4^{2-} and Ca^{2+}. They were highest at NOV and NEU, whereas they were lowest at the two high-elevation sites (CEL, NAT) (Figure 2, Table III).

As a rule, the concentrations in throughfall were much higher than those in bulk precipitation, due to the enrichment of precipitation as it passes through the canopy (Figure 2). Concentrations were higher in throughfall than bulk precipitation for all elements (most clearly K^+ and Mg^{2+}), except for H^+ and, at CEL and NAT, NH_4^+. On these two plots, the concentrations of NO_3^- and SO_4^{2-} were lower in throughfall than in bulk precipitation in some of the sampling years. Lower NH_4^+ concentrations in throughfall than in bulk precipitation were also observed at NOV and ALP in some years. pH in the bulk precipitation and throughfall was lowest at ALP and NOV. The only plots where H^+ concentrations were noticeably higher in throughfall than in bulk precipitation for all sampling years were VOR and BEA. The ranking of the plots according to the solute concentrations was not the same for bulk and throughfall precipitation, which again illustrated the effect of the canopy on precipitation chemistry. Concentrations in throughfall were highest at the plots located on the Central Plateau (especially OTH), the Jura and the Southern Alps (NOV). Concentrations in throughfall were lowest at the high-elevation sites.

TABLE III

Annual precipitation and volume-weighted mean annual element concentrations (μeq l^{-1}), median pH and mean conductivity at 20 °C (μS cm^{-1}) in the open field (bulk precipitation BP) and under the canopy (throughfall TF)

		mm		$[NH_4^+]$		$[NO_3^-]$		$[SO_4^{2-}]$		$[Ca^{2+}]$		$[Mg^{2+}]$		$[K^+]$		$[Na^+]$		$[Cl^-]$		$[H^+]$		Median pH		Conductivity	
Site	Year	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF
Jura																									
BET	99	1627	1469	23.8	30.1	29.6	52.3	22.5	32.0	21.8	51.7	3.6	13.7	4.4	37.7	13.5	18.1	8.6	17.7	11.1	9.3	5.5	5.6	9.6	17.5
	00	1309	1149	21.6	27.0	23.3	43.9	22.1	32.8	23.5	52.9	3.4	14.1	4.0	39.9	9.1	16.9	9.0	18.2	4.3	4.6	5.5	5.8	9.7	19.7
	01	1622	1446	18.5	23.4	18.3	37.9	17.8	25.8	20.8	46.4	3.3	11.7	3.2	31.8	6.5	9.8	6.2	11.2	3.3	2.0	5.8	6.4	7.7	13.8
NEU	98	790	648	46.2	55.8	34.8	63.6	33.7	50.2	21.4	55.3	5.0	19.5	4.8	92.3	14.9	18.5	13.0	27.5	7.1	4.9	5.2	6.1	13.4	32.6
Central Plateau																									
JUS*	98	883	667	24.3	44.5	26.5	30.0	26.1	36.9	22.9	64.6	3.9	34.6	5.3	119.2	10.6	16.7	9.4	24.3	11.2	2.7	5.0	6.0	12.0	30.2
	99	1316	1039	28.4	53.2	32.5	41.8	26.2	36.5	32.5	75.5	4.7	29.1	3.1	98.1	15.3	20.8	14.1	23.1	5.4	2.9	5.8	6.2	10.3	26.9
	00	1042	809	25.0	34.5	27.5	29.2	21.8	31.0	34.9	69.8	5.3	31.0	4.0	81.0	10.7	14.9	13.2	20.0	2.8	1.8	5.7	6.2	10.6	25.2
	01	1224	946	21.6	39.3	22.3	27.6	22.3	30.3	33.1	59.9	4.4	22.6	3.6	75.7	7.9	10.2	7.2	14.4	2.6	0.7	5.9	6.6	8.9	21.3
LAU	97	1214	1033	44.0	51.8	33.3	53.8	34.8	46.6	24.5	41.7	3.8	16.4	4.8	71.4	11.3	14.3	10.6	17.1	9.7	4.8	5.1	5.9	13.5	24.6
	98	1181	970	38.9	55.9	32.9	56.8	31.4	44.0	20.0	46.6	4.4	21.1	3.1	65.6	13.5	17.5	11.3	20.6	9.6	7.0	5.2	5.9	13.5	25.3
	99	1477	1390	41.2	40.2	34.2	50.5	30.1	35.3	38.1	46.0	4.7	17.3	2.7	75.5	16.8	20.6	12.2	17.4	4.4	4.7	5.7	6.0	12.0	21.3
	00	1361	1067	35.6	48.1	31.7	48.1	25.4	35.0	27.3	44.3	4.2	15.0	2.9	51.0	9.9	14.6	10.5	17.5	4.0	2.2	5.7	6.3	11.7	21.3
	01	1536	1297	31.8	35.2	24.3	33.3	22.4	28.4	24.4	39.8	3.5	13.0	3.1	50.0	7.3	10.2	5.9	11.4	2.0	1.4	6.1	6.5	8.7	16.4
OTH	95	1130	854	35.6	70.3	31.1	59.9	31.7	74.3	15.0	59.7	2.8	26.1	3.5	92.5	7.4	13.1	6.1	17.2	13.3	3.7	5.1	5.9	16.1	36.9
	96	1004	731	44.3	89.3	37.5	78.7	34.5	86.3	15.5	64.7	2.9	24.4	3.1	96.2	11.0	17.8	8.9	19.0	11.6	4.8	5.0	6.4	15.0	33.3
	97	870	626	36.4	86.3	29.8	73.1	28.1	73.2	14.9	60.4	3.3	20.8	6.4	91.4	9.7	17.0	9.7	21.2	10.8	2.7	5.2	6.2	11.4	33.5
	98	1024	741	34.1	93.6	27.8	69.6	28.7	71.0	19.6	57.8	4.8	21.5	9.3	87.7	13.1	20.5	13.6	25.5	12.1	4.4	5.1	6.2	12.6	35.1
	99	1356	1011	33.1	67.2	33.0	60.2	25.8	56.8	25.1	58.2	5.7	21.4	6.4	92.4	13.8	21.3	11.2	18.2	5.1	2.3	5.8	6.3	10.8	29.1
	00	1077	776	38.4	77.5	33.5	72.2	28.4	58.8	29.5	61.1	4.1	16.0	3.2	56.8	10.9	17.5	10.6	20.5	3.5	3.6	5.6	6.3	12.0	29.0
	01	1304	982	28.5	53.8	22.6	44.0	21.4	42.7	21.1	51.2	3.7	14.9	4.3	61.0	7.1	11.3	6.2	13.5	2.5	0.8	5.9	6.4	8.7	21.1
VOR	97	943	633	47.8	74.2	32.3	71.8	28.7	62.8	14.8	49.4	3.1	17.9	5.5	87.9	11.1	21.0	8.9	31.2	7.3	30.8	5.2	5.2	11.4	40.1
	98	1234	889	39.3	52.1	26.0	58.1	25.9	49.5	17.2	41.1	3.3	15.6	2.9	56.5	11.9	20.0	10.6	25.4	6.4	12.8	5.2	4.9	11.2	26.4
	99	1342	1030	44.6	52.5	37.0	69.4	26.5	46.1	28.6	52.8	5.3	15.8	3.4	44.4	15.8	22.8	14.1	24.9	6.0	11.4	5.9	5.4	11.3	24.5
	00	1113	835	40.7	72.0	29.8	70.8	25.2	44.5	21.7	49.6	3.3	14.1	3.0	39.8	10.0	17.6	11.3	20.2	3.1	4.4	5.8	5.5	10.9	25.2
	01	1406	987	33.8	43.6	23.8	42.6	20.8	33.5	20.7	44.0	3.4	13.7	3.5	64.9	7.3	13.5	6.9	19.6	1.2	9.1	6.1	5.8	8.5	23.5

(*Continued on next page*)

TABLE III
(Continued)

		mm		$[NH_4^+]$		$[NO_3^-]$		$[SO_4^{2-}]$		$[Ca^{2+}]$		$[Mg^{2+}]$		$[K^+]$		$[Na^+]$		$[Cl^-]$		$[H^+]$		Median pH		Conductivity	
Site	Year	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF
Lower Alps																									
ALP	97	2082	2069	26.3	25.6	21.3	25.8	18.4	19.3	6.4	10.7	1.3	2.7	1.7	11.0	8.1	8.4	5.5	6.0	15.4	10.5	4.8	5.0	9.8	10.2
	98	2093	2027	19.9	19.6	19.0	23.0	16.5	18.0	5.0	10.3	1.2	3.0	1.3	13.1	7.9	9.1	5.6	7.0	16.6	13.5	4.8	4.9	10.2	11.2
BEA	00	1195	1025	24.4	27.1	24.0	42.2	18.6	20.5	29.2	40.3	3.7	8.5	2.8	18.9	8.0	11.9	7.5	13.7	3.3	7.8	5.8	5.2	9.2	15.2
	01	1545	1283	19.0	18.9	16.6	29.9	14.2	15.3	18.7	32.6	2.7	7.1	2.6	15.7	5.1	8.1	4.0	7.5	3.2	4.6	5.9	5.5	6.9	11.4
SCH	99	2440	2119	32.9	36.8	35.0	44.8	22.9	28.1	18.8	46.5	3.2	15.0	2.9	38.2	11.0	13.4	7.0	12.7	9.7	6.4	5.3	5.5	10.6	16.9
	00	2387	2002	33.7	43.2	29.9	44.0	22.3	28.3	22.2	54.6	3.8	14.9	4.6	30.7	7.9	11.7	8.0	13.0	3.0	2.0	5.8	6.2	10.6	19.1
	01	2014	1700	31.5	37.1	26.4	39.4	18.9	25.8	18.8	57.6	3.5	18.5	3.9	37.3	7.3	9.2	5.9	12.4	4.9	2.1	5.8	6.4	9.3	17.4
Alps																									
CEL	00	1153	1114	12.2	9.4	17.5	18.0	17.9	20.4	40.6	39.1	4.4	8.9	3.2	12.8	11.3	13.0	10.3	10.6	6.7	6.4	5.8	5.6	9.4	11.2
	01	761	684	20.2	12.8	18.6	16.1	18.2	18.9	22.7	30.0	3.8	10.0	2.9	10.7	5.6	7.8	5.9	6.4	3.6	4.0	5.6	5.5	8.2	9.8
NAT	99	1037	939	18.9	15.9	26.2	22.3	18.0	15.8	30.9	35.0	6.1	10.5	1.6	5.9	10.6	11.4	8.7	7.5	4.3	4.6	6.0	5.6	7.4	8.4
	00	1245	1170	12.8	9.9	16.4	18.2	16.9	16.4	32.9	35.3	5.4	10.4	2.5	6.4	5.3	6.0	8.9	7.4	5.1	4.5	5.6	5.5	8.5	9.1
	01	893	812	15.2	13.4	17.2	18.1	14.5	15.3	21.7	29.6	5.7	11.5	2.7	7.3	5.2	6.1	5.5	4.6	2.9	3.7	6.0	5.7	7.0	8.5
Southern Alps																									
NOV	97	1654	1401	44.8	44.1	43.6	62.0	42.7	50.6	14.4	32.4	4.1	17.3	2.5	31.9	11.4	14.4	10.5	14.8	28.9	18.5	4.6	4.8	19.2	24.1
	98	2126	1885	52.1	55.3	47.6	67.5	47.0	53.4	16.8	34.7	3.7	13.5	1.8	20.9	11.4	12.4	10.5	12.2	29.9	23.5	4.5	4.5	20.9	24.4
	99	2181	1906	58.5	60.3	48.9	70.2	48.1	56.7	31.9	50.6	6.3	19.6	3.2	40.4	19.2	23.4	14.9	17.9	12.1	10.2	5.3	5.5	17.8	24.3
	00	2771	2435	40.0	38.5	38.5	54.2	36.4	41.2	31.6	46.7	4.7	15.6	3.3	27.8	11.6	15.0	10.7	13.6	10.9	9.6	5.2	5.2	16.8	20.6
	01	1728	1584	57.7	50.8	49.4	67.5	47.1	53.2	33.2	55.1	6.3	19.4	2.8	41.5	11.0	15.3	9.9	14.4	9.2	7.1	5.1	5.9	18.9	24.3
CHI**	01	1865	1768	33.6	40.8	30.5	40.4	31.5	38.9	29.5		4.9		2.7		6.9		5.0		5.9		5.7		12.8	

*Means of both subplots.

**Precipitation amount, nitrogen and sulfate concentrations in winter under the forest canopy were estimated (see paragraph 2.4).

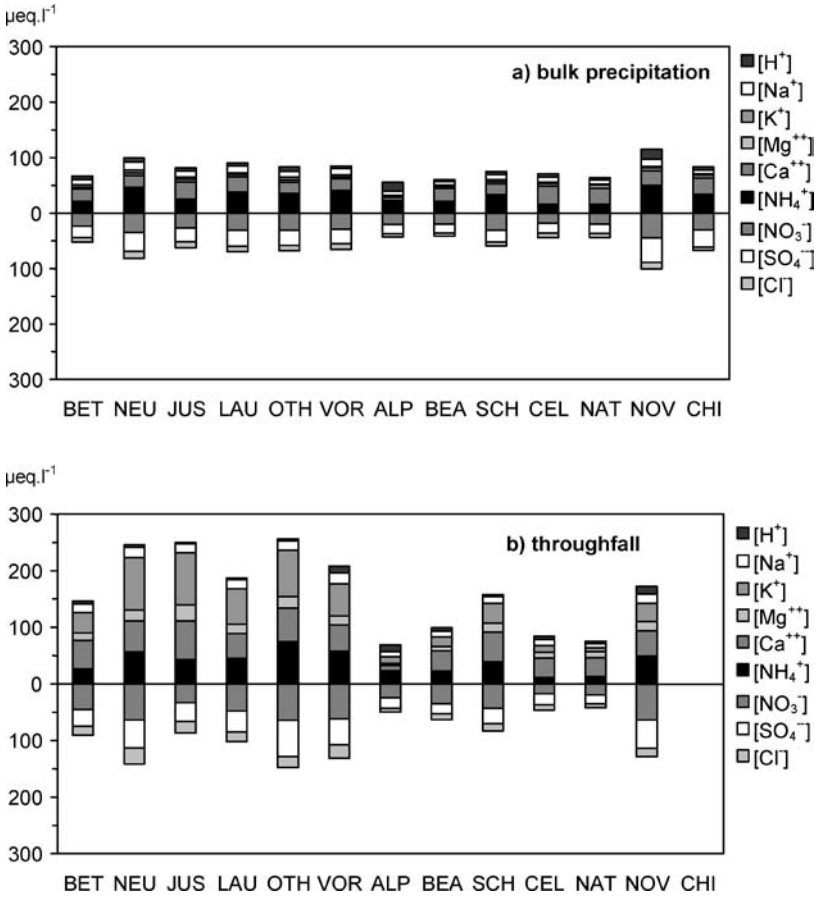

Figure 2. Volume-weighted mean concentrations in bulk precipitation (a) and throughfall (b) (in μeq l^{-1}) on LWF plots. Cations are plotted on the upper part of the y-axis, and anions on the lower part. Variations in concentrations related, e.g., to the time of the year or to the precipitation amounts during the sampling interval may be significant but are not dealt with in this paper.

3.3. FLUXES

Nitrogen and sulfur fluxes in bulk precipitation and throughfall (Table IV, Figure 3) were highest at NOV in the Southern Alps (on average $BP_N = 27.9$ kg ha^{-1} a^{-1}, $TF_N = 29.2$ kg ha^{-1} a^{-1}, $BP_S = 14.7$ kg ha^{-1} a^{-1}, $TF_S = 14.9$ kg ha^{-1} a^{-1}), followed by SCH in the Lower Alps. They were lowest at the high-elevation sites (CEL, NAT), where $BP_N = 4.9$ kg ha^{-1} a^{-1}, $TF_N = 4.0$ kg ha^{-1} a^{-1}, $BP_S = 2.8$ kg ha^{-1} a^{-1}, $TF_S = 2.6$ kg ha^{-1} a^{-1} on average at both plots. The throughfall deposition of N was higher than its bulk deposition on all plots except the two plots at high elevations (CEL, NAT). The difference between throughfall and bulk deposition fluxes was highest at OTH (on average 5.7 kg N ha^{-1} a^{-1}), which was

TABLE IV

Annual element fluxes (kg $ha^{-1}a^{-1}$) in the open field (bulk precipitation BP) and under the canopy (throughfall TF)

		NH_4–N		NO_3–N		Inorg. N		SO_4–S		Ca		Mg		K		Na		Cl		H	
Site	Year	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF
Jura																					
BET	99	5.4	6.2	6.7	10.8	12.2	17.0	5.9	7.5	7.1	15.2	0.7	2.5	2.8	21.7	5.1	6.1	5.0	9.2	0.18	0.14
	00	4.0	4.3	4.3	7.1	8.2	11.4	4.6	6.0	6.1	12.2	0.5	2.0	2.0	17.9	2.7	4.5	4.2	7.4	0.06	0.05
	01	4.2	4.7	4.2	7.7	8.4	12.4	4.6	6.0	6.8	13.4	0.6	2.0	2.0	18.0	2.4	3.3	3.6	5.7	0.05	0.03
NEU	98	5.1	5.1	3.8	5.8	9.0	10.8	4.3	5.2	3.4	7.2	0.5	1.5	1.5	23.4	2.7	2.8	3.7	6.3	0.06	0.03
Central Plateau																					
JUS	98	3.0	4.2	3.3	2.8	6.3	7.0	3.7	4.0	4.0	8.6	0.4	2.8	1.8	31.1	2.2	2.6	2.9	5.8	0.10	0.02
	99	5.2	7.7	6.0	6.1	11.2	13.8	5.5	6.1	8.5	15.7	0.8	3.7	1.6	39.8	4.6	5.0	6.6	8.5	0.07	0.03
	00	3.6	3.9	4.0	3.3	7.7	7.2	3.6	4.0	7.3	11.3	0.7	3.0	1.6	25.6	2.6	2.8	4.9	5.7	0.03	0.01
	01	3.7	5.2	3.8	3.7	7.5	8.9	4.4	4.6	8.1	11.3	0.7	2.6	1.7	28.0	2.2	2.2	3.1	4.8	0.03	0.01
LAU	97	7.5	7.5	5.7	7.8	13.2	15.3	6.8	7.7	5.9	8.6	0.6	2.1	2.3	28.9	3.2	3.4	4.6	6.3	0.12	0.05
	98	6.4	7.6	5.4	7.7	11.9	15.3	6.0	6.9	4.7	9.1	0.6	2.5	1.4	24.9	3.7	3.9	4.7	7.1	0.11	0.07
	99	8.5	7.8	7.1	9.8	15.6	17.7	7.1	7.9	11.3	12.8	0.8	2.9	1.6	41.0	5.7	6.6	6.4	8.6	0.06	0.07
	00	6.8	7.2	6.0	7.2	12.8	14.4	5.6	6.0	7.4	9.4	0.7	1.9	1.6	21.3	3.1	3.6	5.1	6.6	0.05	0.02
	01	6.8	6.4	5.2	6.1	12.1	12.5	5.5	5.9	7.5	10.3	0.7	2.0	1.8	25.3	2.6	3.0	3.2	5.2	0.03	0.02
OTH	95	5.6	8.4	4.9	7.2	10.6	15.6	5.7	10.2	3.4	10.2	0.4	2.7	1.6	30.9	1.9	2.6	2.4	5.2	0.15	0.03
	96	6.2	9.1	5.3	8.1	11.5	17.2	5.6	10.1	3.1	9.5	0.4	2.2	1.2	27.5	2.5	3.0	3.2	4.9	0.12	0.04
	97	4.4	7.6	3.6	6.4	8.1	14.0	3.9	7.4	2.6	7.6	0.4	1.6	2.2	22.4	1.9	2.5	3.0	4.7	0.09	0.02
	98	4.9	9.7	4.0	7.2	8.9	16.9	4.7	8.4	4.0	8.6	0.6	1.9	3.7	25.4	3.1	3.5	4.9	6.7	0.12	0.03
	99	6.3	9.5	6.3	8.5	12.5	18.0	5.6	9.2	6.8	11.8	0.9	2.6	3.4	36.5	4.3	5.0	5.4	6.5	0.07	0.02
	00	5.8	8.4	5.0	7.9	10.8	16.3	4.9	7.3	6.4	9.5	0.5	1.5	1.4	17.2	2.7	3.1	4.0	5.7	0.04	0.03
	01	5.2	7.4	4.1	6.0	9.3	13.4	4.5	6.7	5.5	10.1	0.6	1.8	2.2	23.4	2.1	2.6	2.9	4.7	0.03	0.01
VOR	97	6.3	6.6	4.3	6.4	10.6	12.9	4.3	6.4	2.8	6.2	0.4	1.4	2.0	21.7	2.4	3.1	3.0	7.0	0.07	0.20
	98	6.8	6.5	4.5	7.2	11.3	13.7	5.1	7.1	4.2	7.3	0.5	1.7	1.4	19.6	3.4	4.1	4.6	8.0	0.08	0.11
	99	8.4	7.6	7.0	10.0	15.3	17.6	5.7	7.6	7.7	10.9	0.9	2.0	1.8	17.9	4.9	5.4	6.7	9.1	0.08	0.12
	00	6.3	8.4	4.6	8.3	11.0	16.7	4.5	6.0	4.8	8.3	0.4	1.4	1.3	13.0	2.6	3.4	4.5	6.0	0.03	0.04
	01	6.7	6.0	4.7	5.9	11.3	11.9	4.7	5.3	5.8	8.7	0.6	1.6	1.9	25.1	2.4	3.1	3.5	6.9	0.02	0.09

(*Continued on next page*)

TABLE IV
(Continued)

		NH_4–N		NO_3–N		Inorg. N		SO_4–S		Ca		Mg		K		Na		Cl		H	
Site	Year	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF
Lower Alps																					
ALP	97	7.7	7.4	6.2	7.5	13.9	14.9	6.1	6.4	2.7	4.4	0.3	0.7	1.4	8.9	3.9	4.0	4.0	4.4	0.32	0.22
	98	5.8	5.6	5.6	6.5	11.4	12.1	5.5	5.8	2.1	4.2	0.3	0.7	1.1	10.4	3.8	4.2	4.1	5.0	0.35	0.27
BEA	00	4.1	3.9	4.0	6.1	8.1	9.9	3.6	3.4	7.0	8.3	0.5	1.1	1.3	7.6	2.2	2.8	3.2	5.0	0.04	0.08
	01	4.1	3.4	3.6	5.4	7.7	8.8	3.5	3.2	5.8	8.4	0.5	1.1	1.6	7.9	1.8	2.4	2.2	3.4	0.05	0.06
SCH	99	11.2	10.9	12.0	13.3	23.2	24.2	9.0	9.5	9.2	19.7	1.0	3.9	2.8	31.6	6.2	6.5	6.1	9.5	0.24	0.14
	00	11.3	12.1	10.0	12.3	21.3	24.4	8.5	9.1	10.6	21.9	1.1	3.6	4.3	24.0	4.3	5.4	6.8	9.2	0.07	0.04
	01	8.9	8.8	7.4	9.4	16.3	18.2	6.1	7.0	7.6	19.6	0.9	3.8	3.1	24.8	3.4	3.6	4.2	7.5	0.10	0.04
Alps																					
CEL	00	2.0	1.5	2.8	2.8	4.8	4.3	3.3	3.7	9.4	8.7	0.6	1.2	1.5	5.6	3.0	3.3	4.2	4.2	0.08	0.07
	01	2.1	1.2	2.0	1.5	4.1	2.8	2.2	2.1	3.5	4.1	0.3	0.8	0.9	2.9	1.0	1.2	1.6	1.6	0.03	0.03
NAT	99	2.7	2.1	3.8	2.9	6.6	5.0	3.0	2.4	6.4	6.6	0.8	1.2	0.7	2.1	2.5	2.5	3.2	2.5	0.04	0.04
	00	2.2	1.6	2.9	3.0	5.1	4.6	3.4	3.1	8.2	8.3	0.8	1.5	1.2	2.9	1.5	1.6	3.9	3.1	0.06	0.05
	01	1.9	1.5	2.2	2.1	4.1	3.6	2.1	2.0	3.9	4.8	0.6	1.1	0.9	2.3	1.1	1.1	1.8	1.3	0.03	0.03
Southern Alps																					
NOV	97	10.4	8.7	10.1	12.2	20.5	20.8	11.3	11.4	4.8	9.1	0.8	3.0	1.6	17.5	4.3	4.6	6.1	7.3	0.48	0.26
	98	15.5	14.6	14.2	17.8	29.7	32.4	16.0	16.1	7.1	13.1	1.0	3.1	1.5	15.4	5.6	5.4	7.9	8.2	0.64	0.44
	99	17.9	16.1	14.9	18.7	32.8	34.8	16.8	17.3	13.9	19.3	1.7	4.5	2.8	30.1	9.6	10.3	11.5	12.1	0.26	0.20
	00	15.5	13.1	14.9	18.5	30.4	31.6	16.2	16.1	17.5	22.7	1.6	4.6	3.6	26.5	7.4	8.4	10.5	11.7	0.30	0.23
	01	14.0	11.3	12.0	15.0	25.9	26.2	13.1	13.5	11.5	17.4	1.3	3.7	1.9	25.7	4.4	5.6	6.0	8.1	0.16	0.11
CHI**	01	8.8	*10.1*	8.0	*10.0*	16.7	*20.1*	9.4	*11.0*	11.0	–	1.1	–	2.0	–	3.0	–	3.3	–	0.11	–

**Nitrogen and sulfate fluxes in winter under forest canopy were estimated (see paragraph 2.4).

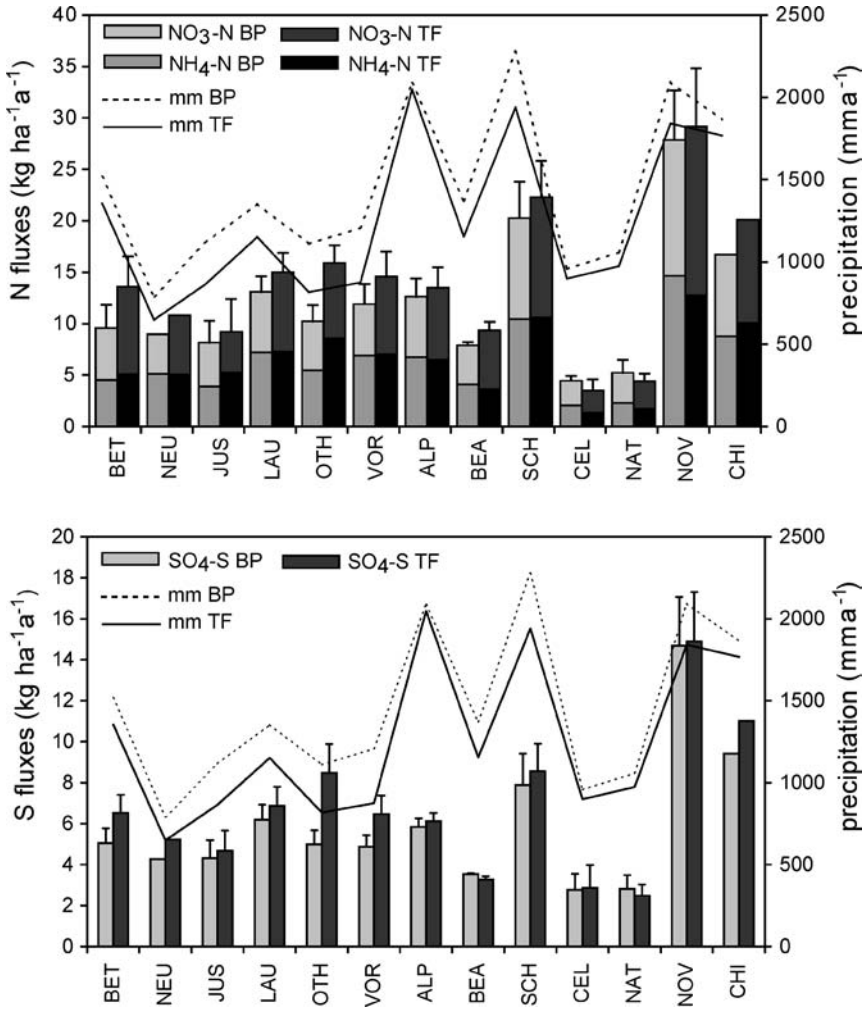

Figure 3. Mean annual inorganic nitrogen (NH_4–N + −N) (top) and sulfate (SO_4–S) (bottom) fluxes (kg ha^{-1} a^{-1}) in the open area (BP) and in the forest stand (TF). Mean annual precipitation in the open area and in the stand (mm a^{-1}) is also shown.

also the plot with the highest interception. It was rather low for the other plots. The deposition pattern for S was similar to the pattern for N. Two plots (NAT, BEA) showed lower SO_4^{2-} fluxes in throughfall than in bulk deposition.

Bulk deposition of Ca^{2+} and Mg^{2+} was highest at NOV, and lowest at ALP (Table IV). Throughfall enrichment in Ca^{2+} was highest at SCH and BET, and throughfall deposition of Ca^{2+} and Mg^{2+} was highest in NOV and SCH. It was lowest at ALP. The year-to-year variation in Ca^{2+} deposition could be quite large (NOV, CEL). Na^+ and Cl^- fluxes in both bulk precipitation and throughfall were highest in NOV.

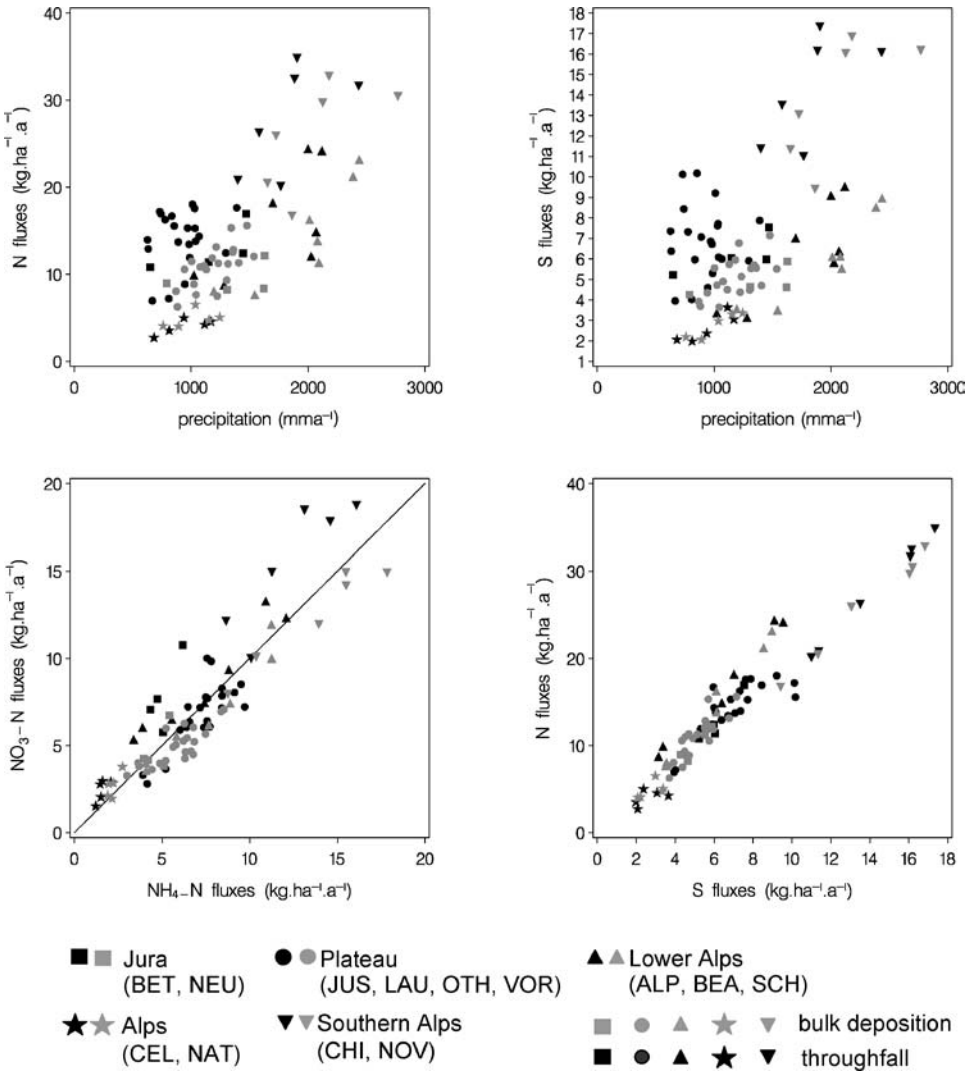

Figure 4. Relationships on each LWF plot between: (a) annual inorganic nitrogen (NH_4–N + NO_3–N) fluxes and annual precipitation in the open area and in the forest stand; (b) annual sulfate (SO_4–S) fluxes and annual precipitation in the open area and in the forest stand; (c) NH_4–N and NO_3–N annual fluxes; (d) N and S annual fluxes.

The annual N and SO_4^{2-} depositions positively correlated with the annual precipitation amounts (Figure 4) at the regional level (plot-to-plot variation), as well as at the plot level (year-to-year variation for each plot). Plots with high annual precipitation tended to have higher bulk deposition fluxes, even though the differences in pollution climate between plots were still apparent for plots with similar precipitation amounts but different element fluxes (e.g. NOV, SCH and ALP). The correlation was stronger for bulk deposition than for throughfall. N and SO_4^{2-}

concentrations were closely correlated, as were N and SO_4^{2-} depositions. NH_4^+ and NO_3^- concentrations and depositions were also significantly correlated. The contribution of NH_4^+ to inorganic N deposition varied from 41% (CEL in 2000) to 61% (VOR in 1998) in bulk deposition and from 34% (CEL in 2000) to 60% (JUS in 1998) in throughfall.

3.4. Estimates of the components of atmospheric deposition compared with modeled deposition

The estimated wet and dry components of atmospheric deposition, as well as the estimated canopy leaching or uptake, are given in Table V for each sampling year. Negative dry SO_4^{2-} deposition estimates may have to be interpreted as SO_4^{2-} uptake from the canopy (NAT in 1999). NOV was clearly the plot with the highest total loads of N and S, followed by SCH.

Estimated wet deposition of N (corrected bulk deposition, $WD_{N(LWF)}$) and modeled wet deposition ($WD_{N(mod)}$) were closely correlated ($r = 0.87$, $p < 0.001$, $n = 13$; Table VI, Figure 5). The highest difference between modeled and LWF values were observed at ALP, where $WD_{N(mod)}$ exceeded $WD_{N(LWF)}$ by 6.3 kg N ha^{-1} a^{-1}. The LWF estimates for dry deposition of N ($DD_{N(LWF)}$) also correlated with the modeled values ($DD_{N(mod)}$), though less closely ($r = 0.70$, $p < 0.05$, $n = 12$). The correlation between LWF total deposition ($TD_{N(LWF)}$) and modeled total deposition ($TD_{N(mod)}$) was highly significant ($r = 0.84$, $p < 0.001$, $n = 12$). $DD_{N(mod)}$, however, systematically exceeded $DD_{N(LWF)}$ and $TD_{N(mod)}$ $TD_{N(LWF)}$, especially at ALP, with the exception of NOV.

The correlation between sulfur WD derived from BP values ($WD_{S(LWF)}$) and the modeled deposition for S ($WD_{S(mod)}$) was also significant ($r = 0.75$, $p < 0.01$, $n = 13$; Table VI, Figure 5). The main differences between $WD_{S(LWF)}$ and $WD_{S(mod)}$ were observed at ALP ($WD_{S(mod)}$ exceeded $WD_{S(LWF)}$ by 2.9 kg ha^{-1} a^{-1}) and NOV ($WD_{S(mod)}$ was lower than $WD_{S(LWF)}$ by 5.2 kg ha^{-1} a^{-1}). The correlation between LWF dry deposition for S ($DD_{S(LWF)}$) and modeled dry deposition ($DD_{S(mod)}$) was somewhat weaker ($r = 0.69$, $p < 0.05$, $n = 12$), as was the correlation between LWF and modeled total deposition for S ($r = 0.70$, $p < 0.05$, $n = 12$ between $TD_{S(LWF)}$ and $TD_{S(mod)}$). $DD_{S(mod)}$ exceeded $DD_{S(LWF)}$ for the four plots located on the Plateau and NEU. $TD_{S(mod)}$ was higher than $TD_{S(LWF)}$ for all plots except NOV.

3.5. Critical loads for nitrogen

The SMB approach yielded critical loads for N which was within the range of critical loads empirically established for the managed plots (Table VII). On unmanaged plots, where no N is removed by wood harvesting ($U_N = 0$), the SMB critical loads were lower than the empirical ones. $TD_{N(mod)}$ exceeded the SMB critical loads on

TABLE V

Estimated components of atmospheric deposition (WD, DD), canopy uptake (CU) of nitrogen and canopy leaching (Cle) of base cations (in kg $ha^{-1}a^{-1}$)

		NH_4–N			NO_3–N			Inorg. N				S		Ca			Mg			K			Na		Cl	
Site	Year	WD	DD	CU	WD	DD	CU	WD	DD	CU	TD	WD	DD	WD	DD	Cle	WD	DD	Cle	WD	DD	Cle	WD	DD	WD	DD
Jura																										
BET	1999	4.8	4.5	3.1	5.6	6.1	0.9	10.4	10.6	4.1	21.0	4.9	2.6	4.9	3.7	6.6	0.5	0.3	1.6	1.9	1.5	18.3	4.1	2.0	4.1	5.2
	2000	3.5	2.0	1.2	3.5	3.8	0.3	7.1	5.8	1.5	12.9	3.9	2.1	4.2	5.8	2.1	0.4	0.5	1.1	1.4	2.0	14.6	2.2	2.3	3.4	4.0
	2001	3.7	4.7	3.8	3.5	5.2	1.0	7.2	10.0	4.8	17.2	3.9	2.1	4.7	4.5	4.3	0.5	0.4	1.2	1.3	1.4	15.3	2.0	1.3	2.9	2.8
NEU	1998	4.5	4.5	4.0	3.2	3.3	0.8	7.7	7.8	4.7	15.6	3.6	1.6	2.3	1.1	3.7	0.4	0.1	1.0	1.0	0.5	21.9	2.2	0.6	3.0	3.3
Central Plateau																										
JUS	1998	2.7	2.8	1.4	2.7	0.2	0.2	5.4	3.1	1.5	8.5	3.1	0.8	2.8	2.0	3.8	0.3	0.2	2.3	1.2	1.0	28.9	1.8	0.8	2.4	3.4
	1999	4.7	4.3	1.2	5.0	1.3	0.2	9.6	5.6	1.4	15.2	4.7	1.4	5.9	3.3	6.5	0.5	0.3	2.9	1.1	0.7	38.1	3.7	1.2	5.4	3.1
	2000	3.2	2.3	1.6	3.3	0.2	0.2	6.6	2.5	1.8	9.1	3.1	1.0	5.0	2.9	3.4	0.5	0.2	2.3	1.1	0.7	23.8	2.1	0.7	4.0	1.7
	2001	3.3	4.7	2.8	3.2	0.8	0.3	6.5	5.6	3.2	12.0	3.7	0.9	5.6	2.5	3.2	0.5	0.2	1.9	1.2	0.6	26.3	1.8	0.4	2.6	2.2
LAU	1997	6.7	5.5	4.7	4.7	3.9	0.8	11.4	9.4	5.5	20.8	5.7	2.0	4.1	2.3	2.2	0.4	0.2	1.5	1.5	0.9	26.4	2.6	0.8	3.8	2.5
	1998	5.7	4.9	3.1	4.5	3.7	0.5	10.2	8.6	3.6	18.9	5.0	1.9	3.3	1.8	4.0	0.5	0.2	1.8	1.0	0.6	23.4	3.0	0.9	3.9	3.2
	1999	7.6	5.8	5.5	5.9	5.1	1.2	13.5	10.9	6.7	24.4	6.0	1.9	7.8	5.2	(−0.2)	0.6	0.4	1.9	1.1	0.8	39.2	4.6	2.0	5.2	3.4
	2000	6.0	4.3	3.2	5.0	2.7	0.5	11.1	7.0	3.7	18.1	4.7	1.3	5.1	3.4	0.9	0.5	0.3	1.2	1.0	0.7	19.5	2.5	1.1	4.2	2.5
	2001	6.1	4.6	4.3	4.3	2.4	0.7	10.4	7.0	5.0	17.5	4.6	1.3	5.2	3.6	1.5	0.5	0.3	1.3	1.2	0.9	23.2	2.1	0.9	2.6	2.6
OTH	1995	5.0	7.9	4.5	4.1	3.7	0.6	9.1	11.6	5.1	20.7	4.8	5.4	2.3	2.2	5.6	0.3	0.2	2.2	1.0	1.1	28.8	1.6	1.0	2.0	3.2
	1996	5.5	8.1	4.5	4.4	4.3	0.7	9.9	12.4	5.1	22.3	4.7	5.5	2.1	1.5	5.8	0.3	0.2	1.7	0.8	0.6	26.0	2.1	0.9	2.6	2.3
	1997	3.9	7.8	4.2	3.0	4.0	0.6	7.0	11.8	4.7	18.7	3.3	4.1	1.8	1.5	4.3	0.3	0.2	1.1	1.5	1.3	19.6	1.6	0.9	2.5	2.3
	1998	4.3	10.1	4.7	3.3	4.5	0.6	7.7	14.6	5.3	22.2	4.0	4.5	2.8	1.8	4.0	0.4	0.2	1.3	2.5	1.7	21.2	2.5	1.0	4.0	2.7
	1999	5.6	8.5	4.5	5.2	4.0	0.7	10.8	12.5	5.2	23.3	4.7	4.5	4.7	3.1	4.0	0.7	0.4	1.6	2.3	1.6	32.6	3.5	1.5	4.4	2.1
	2000	5.2	6.7	3.4	4.2	4.2	0.5	9.3	10.9	4.0	20.2	4.1	3.2	4.4	3.1	2.0	0.4	0.2	0.9	0.9	0.7	15.7	2.2	1.0	3.3	2.3
	2001	4.6	6.9	4.1	3.4	3.2	0.6	8.1	10.1	4.7	18.1	3.8	2.9	3.8	2.8	3.5	0.4	0.3	1.1	1.5	1.1	20.8	1.7	0.8	2.4	2.3
VOR	1997	5.6	2.3	1.4	3.5	3.0	0.2	9.2	5.4	1.6	14.5	3.7	2.7	1.9	1.6	2.7	0.3	0.2	0.9	1.4	1.2	19.2	2.0	1.1	2.4	4.6
	1998	6.0	3.5	3.0	3.7	4.1	0.6	9.8	7.5	3.6	17.3	4.3	2.8	2.9	2.2	2.2	0.4	0.2	1.1	0.9	0.8	18.0	2.7	1.3	3.8	4.2
	1999	7.5	4.4	4.3	5.8	5.2	0.9	13.2	9.5	5.2	22.8	4.8	2.8	5.3	3.2	2.4	0.6	0.3	1.0	1.2	0.8	15.9	4.0	1.4	5.5	3.6
	2000	5.6	5.6	2.9	3.8	4.9	0.5	9.5	10.5	3.3	20.0	3.8	2.2	3.3	3.1	1.9	0.3	0.3	0.8	0.9	0.8	11.3	2.1	1.3	3.7	2.3
	2001	5.9	2.0	1.9	3.9	2.3	0.3	9.8	4.3	2.2	14.1	4.0	1.4	4.0	3.5	1.2	0.4	0.3	0.9	1.3	1.2	22.6	1.9	1.1	2.8	4.0

(*Continued on next page*)

TABLE V
(Continued)

		$NH_4 - N$			$NO_3 - N$			Inorg. N				S		Ca			Mg			K			Na		Cl	
Site	Year	WD	DD	CU	WD	DD	CU	WD	DD	CU	TD	WD	DD	WD	DD	Cle	WD	DD	Cle	WD	DD	Cle	WD	DD	WD	DD
Lower Alps																										
ALP	1997	6.8	2.7	2.1	5.2	2.7	0.4	12.0	5.4	2.5	17.4	5.2	1.2	1.8	0.9	1.7	0.2	0.1	0.3	1.0	0.5	7.4	3.2	0.9	3.3	1.1
	1998	5.2	1.5	1.1	4.6	2.1	0.2	9.8	3.6	1.3	13.4	4.7	1.2	1.4	0.9	1.9	0.2	0.1	0.4	0.7	0.5	9.2	3.1	1.2	3.4	1.6
BEA	2000	3.6	1.6	1.4	3.3	3.1	0.4	7.0	4.7	1.7	11.7	3.0	0.4	4.8	4.1	(−0.6)	0.4	0.3	0.4	0.9	0.8	5.9	1.8	1.0	2.6	2.4
	2001	3.7	1.4	1.7	3.0	2.8	0.4	6.6	4.2	2.1	10.9	3.0	0.2	4.0	3.7	0.7	0.4	0.3	0.4	1.1	1.0	5.8	1.5	0.9	1.8	1.6
SCH	1999	10.0	5.2	4.3	9.9	4.2	0.9	19.9	9.5	5.2	29.4	7.5	2.0	6.3	3.4	10.0	0.7	0.3	2.9	1.9	1.1	28.7	5.0	1.5	5.0	4.5
	2000	10.0	6.2	4.1	8.3	4.7	0.7	18.3	10.9	4.8	29.3	7.2	1.9	7.3	5.9	8.6	0.8	0.6	2.3	2.9	2.5	18.7	3.5	1.9	5.5	3.7
	2001	7.9	8.0	7.1	6.2	4.5	1.3	14.1	12.5	8.4	26.6	5.1	1.9	5.2	2.8	11.5	0.6	0.3	2.9	2.1	1.2	21.5	2.7	0.9	3.5	4.0
Alps																										
CEL	2000	1.8	0.7	1.0	2.3	0.8	0.3	4.1	1.5	1.3	5.6	2.8	0.9	6.5	4.0	(−1.7)	0.5	0.2	0.5	1.0	0.6	3.9	2.4	0.9	3.5	0.7
	2001	1.9	(−0.3)	0.4	1.6	(−0.0)	0.1	3.6	(−0.3)	0.5	3.2	1.9	0.2	2.4	2.0	(−0.2)	0.3	0.2	0.4	0.6	0.5	1.8	0.8	0.4	1.3	0.3
NAT	1999	2.4	0.4	0.7	3.2	(−0.1)	0.2	5.6	0.3	0.9	5.9	2.5	(−0.1)	4.4	1.8	0.4	0.6	0.2	0.5	0.4	0.2	1.5	2.1	0.4	2.6	(−0.1)
	2000	2.0	0.6	1.0	2.4	0.9	0.3	4.4	1.5	1.3	5.9	2.8	0.2	5.7	3.0	(−0.4)	0.6	0.3	0.6	0.8	0.5	1.6	1.2	0.4	3.2	(−0.2)
	2001	1.7	0.5	0.7	1.8	0.4	0.1	3.5	0.9	0.8	4.4	1.7	0.2	2.7	1.4	0.7	0.5	0.2	0.5	0.6	0.4	1.3	0.9	0.3	1.4	(−0.1)
Southern Alps																										
NOV	1997	9.2	2.0	2.5	8.4	4.4	0.6	17.6	6.3	3.1	24.0	9.5	1.9	3.3	1.8	4.0	0.6	0.3	2.1	1.1	0.6	15.8	3.5	1.1	5.0	2.3
	1998	13.8	3.9	3.1	11.8	6.7	0.6	25.6	10.6	3.7	36.1	13.5	2.7	4.9	2.0	6.2	0.7	0.2	2.2	1.0	0.4	13.9	4.5	0.9	6.5	1.7
	1999	15.9	6.0	5.8	12.4	7.5	1.1	28.3	13.5	7.0	41.8	14.1	3.2	9.6	5.3	4.4	1.2	0.6	2.7	1.9	1.1	27.2	7.8	2.5	9.5	2.6
	2000	13.8	3.7	4.4	12.4	7.1	1.0	26.2	10.8	5.4	37.0	13.6	2.5	12.1	7.9	2.8	1.2	0.6	2.8	2.4	1.7	22.4	6.0	2.4	8.6	3.1
	2001	12.4	2.8	4.0	9.9	5.9	0.9	22.4	8.8	4.9	31.1	11.0	2.5	7.9	6.7	2.8	1.0	0.7	2.1	1.3	1.2	23.2	3.6	2.0	5.0	3.2
CHI	2001	7.8	—	—	6.6	—	—	14.4	—	—	—	7.9	*3.1*	7.6	—	—	0.8	—	—	1.3	—	—	2.4	—	2.7	—

TABLE VI

Mean annual nitrogen (NO_3–N + NH_4–N) and sulfur fluxes based on measurements on the LWF plots (wet deposition WD, throughfall TF, estimated dry deposition DD and total deposition TD) and modeled wet deposition (WD) of nitrogen (NO_3–N + NH_4−N) and sulfate, modeled DD of nitrogen (NO_x and NH_y) and sulfur dioxide (SO_2)

	N (NO_3−N + NH_4−N) fluxes (kg N $ha^{-1}a^{-1}$)								S fluxes (kg S $ha^{-1}a^{-1}$)					
	LWF					Modeled deposition			LWF			Modeled deposition		
	WD	DD	TD	TF	TD/TF	WD	DD	TD	WD	DD	TD	WD	DD	TD
Jura														
BET	8.2	8.8	17.0	13.6	1.3	11.7	9.9	21.6	4.2	2.3	6.5	5.3	2.2	7.5
NEU	7.7	7.8	15.6	10.8	1.4	8.1	9.6	17.8	3.6	1.6	5.2	3.7	5.0	8.7
Central Plateau														
JUS	7.0	4.2	11.2	9.2	1.2	7.6	10.1	17.7	3.6	1.0	4.7	3.4	4.7	8.2
LAU	11.3	8.6	19.9	15.0	1.3	9.4	14.4	23.8	5.2	1.7	6.9	4.3	2.7	7.0
OTH	8.8	12.0	20.8	15.9	1.3	8.8	19.6	28.4	4.2	4.3	8.5	4.0	5.8	9.8
VOR	10.2	7.5	17.8	14.6	1.2	8.7	19.9	28.6	4.1	2.4	6.5	3.9	5.3	9.2
Lower Alps														
ALP	10.9	4.5	15.4	13.5	1.1	17.2	11.1	28.3	4.9	1.2	6.1	7.8	1.3	9.2
BEA	6.8	4.5	11.3	9.4	1.2	8.9	9.6	18.5	3.0	0.3	3.3	4.1	0.4	4.5
SCH	17.3	11.1	28.4	22.3	1.3	14.0	13.9	27.9	6.6	2.0	8.6	6.4	3.2	9.5
Alps														
CEL	3.7	0.7	4.4	3.5	1.3	6.4	5.6	12.0	2.3	0.5	2.8	3.0	0.7	3.7
NAT	4.5	0.9	5.4	4.4	1.2	6.4	3.2	9.6	2.4	0.1	2.5	3.0	0.8	3.8
S. Alps														
NOV	24.0	10.0	34.0	29.2	1.2	20.8	8.8	29.6	12.3	2.6	14.9	7.1	2.2	9.4
CHI	13.9			20.1		13.5	7.5	21.0	7.6	3.4	11.0	7.2	2.1	9.3

Note. Years of reference for modeled nitrogen deposition: 2000 north of the Alps, 1993–2000 south of the Alps.
Years of reference for modeled wet deposition of sulfur: 1997–1999; for dry deposition of SO_2: 2000.
Estimated LWF WD: BP. correction factor.
Estimated LWF TD of N: TD after the canopy budget model.
Estimated LWF Deposition of S: TD = TF, DD = TD-WD.

all plots, whereas $TD_{N(LWF)}$ was below the SMB critical load on the two alpine plots (CEL, NAT), ALP, and the managed subplot of JUS. NOV, SCH, and, to a lesser extent, CHI were the three plots where throughfall, which provides a lower estimate of total N deposition, exceeded both SMB and empirical critical loads.

4. Discussion

4.1. Regional distribution of atmospheric deposition

At the high-elevation sites (CEL and NAT), which are remote from pollution sources, measured atmospheric deposition was low (only a little higher than what

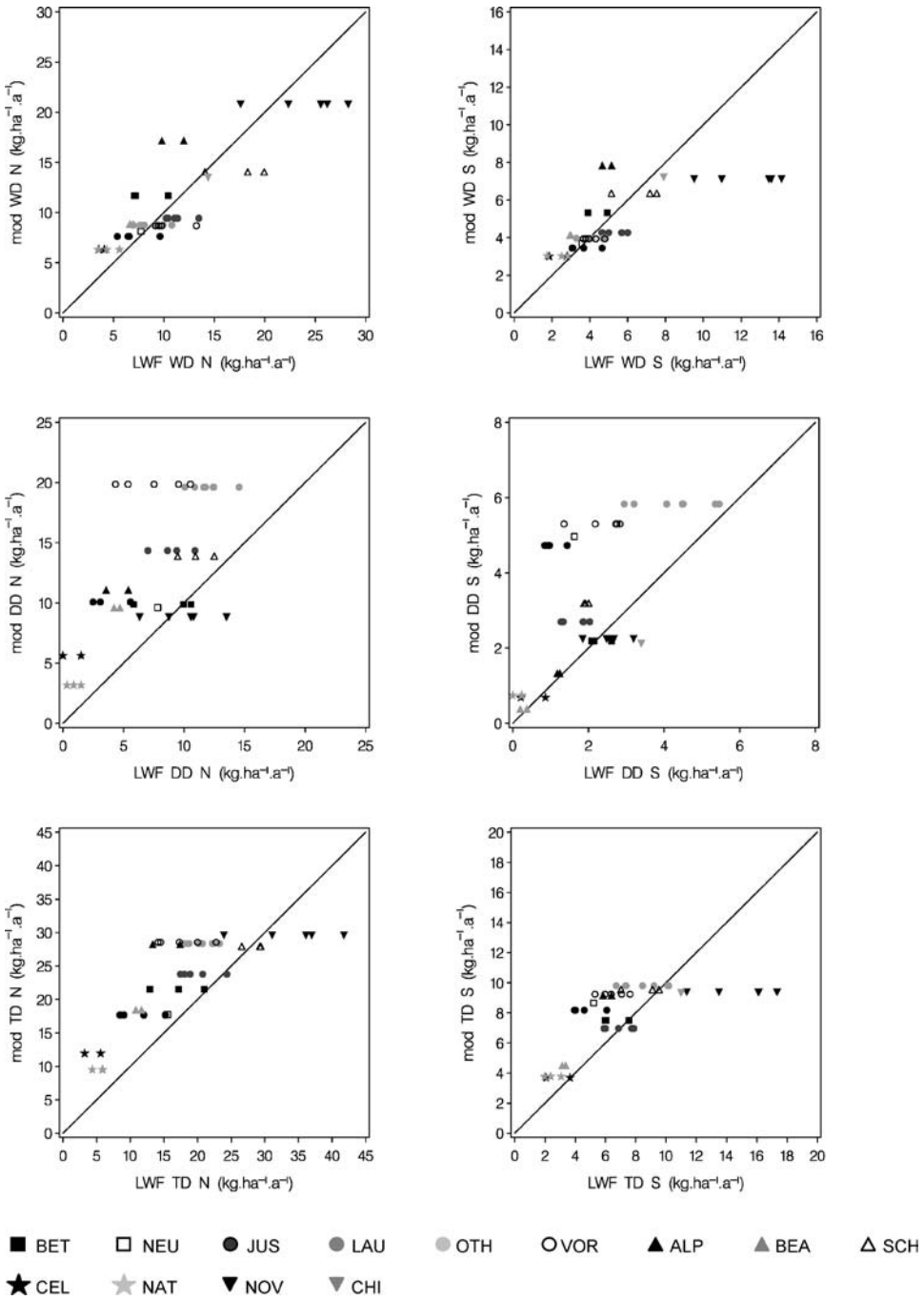

Figure 5. Modeled deposition versus LWF estimates. Left: N deposition (wet deposition WD, dry deposition DD, total deposition TD). Right: S deposition (WD, DD, TD).

TABLE VII
Empirical critical loads for nitrogen (CL_N) and calculated critical loads using the steady state mass balance (SMB) method for the LWF plots

	U_N	I_N	le(acc)$_N$	fde	SMB CL_N	Empirical CL_N	TF_N	$TD_{N(LWF)}$	$TD_{N(mod)}$
BET	0	4.3	3.1	0.3	8.8	15–20	13.6	17.0	21.6
NEU	0	3.2	3.9	0.3	8.7	15–20	10.8	15.6	17.8
JUS managed	7.1	3.0	4.0	0.3	15.9	10–20	9.2	11.2	17.7
JUS unmanaged	0	3.0	4.0	0.3	8.7	10–20	9.2	11.2	17.7
LAU	7.1	3.6	3.6	0.3	15.9	10–20	15.0	19.9	23.8
OTH	7.1	3.0	4.0	0.5	18.1	10–20	15.9	20.8	28.4
VOR	4.3	3.0	4.0	0.3	13.0	7–20	14.6	17.8	28.6
ALP	2.2	4.3	3.1	0.7	16.9	15–20	13.5	15.4	28.3
BEA	2.2	5.0	2.7	0.3	10.9	7–20	9.4	11.3	18.5
SCH	4.3	3.5	3.7	0.3	13.0	10–20	22.3	28.4	27.9
CEL	1.5	5.0	2.2	0.3	9.6	7–20	3.5	4.4	12.0
NAT	0	5.0	2.1	0.3	8.1	15–20	4.4	5.4	9.6
NOV	0	3.9	3.4	0.3	8.8	10–20	29.2	34.0	29.6
CHI	0.8	4.7	2.8	0.3	9.6	7–20	*20.1*		21.0

Note. The SMB method uses the following equation: $CL_N = U_N + I_N + le(acc)_N/(1\text{-fde})$ (in Rihm 1996) where U_N is the amount of *N* removed by wood harvesting, fde the denitrification fraction, le(acc)$_N$ the acceptable total leaching from the rooting zone, I_N the acceptable immobilization rate of N in soil organic matter. All values (except fde) are in kg N $ha^{-1}a^{-1}$.

deposition levels would be in the absence of anthropogenic sources) and below the critical loads for N. Similar low deposition rates for N were measured in the second half of the 1980s in the Alps in Davos (Kloeti *et al*., 1989), but the throughfall deposition of S was higher in Davos (10 kg S ha^{-1} a^{-1} under a spruce canopy) than that measured at CEL and NAT. Different stand characteristics, the vicinity of the town of Davos, or a general decrease in S deposition might be possible explanations. At CEL and NAT, TF fluxes were only slightly higher than WD fluxes (derived from BP fluxes) for N and S, indicating a very low contribution of dry deposition to the total deposition and/or canopy uptake of these elements. For N this pattern is typical of remote areas (Lovett and Lindberg, 1993). At NAT the availability of N for vegetation appears to be low as the carbon nitrogen ratio (C:N) in the soil is very high and the decomposition rate of organic matter slow (Dobbertin *et al*., 2001). At CEL, the C:N ratio in the soil organic matter is lower, but the C:N in the soil solution is high (Pannatier, WSL, personal communication). Hence, atmospheric nitrogen is likely to be readily taken up by the canopy on these plots.

On the Central Plateau, deposition of N and S was moderate. Mean annual SO_4^{2-} concentrations in WD at OTH and VOR were very close to those measured in 1997–1999 at the EMEP stations on the Plateau (Dübendorf, Payerne, Tänikon) (NABEL, 2000). Likewise, similar SO_4^{2-} concentrations in WD were measured at BET and

the EMEP station of Chaumont (Jura). The LWF measurements of S deposition were substantially lower than the deposition rates measured on the Lägern, in the lowlands near Zurich at the end of the 1980s (Kloeti *et al*., 1989), both in the open area (10 kg S ha^{-1} a^{-1} in WD on the Lägern) and in throughfall (15.1 kg ha^{-1} a^{-1} under beech canopy, 40.3 kg ha^{-1} a^{-1} under spruce canopy). In 2001, Burkard *et al*. (2003) estimated the wet deposition of sulfur on the Lägern to be about 4.2 kg ha^{-1} a^{-1}, which is within the range of the LWF values. This is in agreement with the decrease in the wet deposition of sulfur also observed at Dübendorf and Payerne over the period 1985–1999 (NABEL, 2000) and the general reduction in S emissions in Switzerland (FOEFL (Publisher), 2002).

In contrast, the N deposition in the open areas on the LWF plots on the Plateau differed little from the wet deposition on the Lägern in the 1980s (9.1 kg N ha^{-1} a^{-1}; Kloeti *et al*., 1989), and was only slightly higher than in 2001 at this latter site (about 6.9 kg N ha^{-1} a^{-1}; Burkard *et al*., 2003). Under a spruce canopy, throughfall deposition was substantially higher on the Lägern (35.7 kg N ha^{-1} a^{-1}) than on any of the LWF plots located on the Plateau, but the N throughfall fluxes under a beech canopy on the Lägern (19.3 kg N ha^{-1} a^{-1}) were only 1.3 kg N ha^{-1} a^{-1} higher than the highest TF flux at OTH (measured in 1999) in a similar stand. Air concentrations of nitrogen oxides decreased from the end of the 1980s to 1994 and appear to be stabilizing. There do not seem, however, to be such clear trends for NO_3^- and NH_4^+ concentrations in wet deposition (NABEL, 2002). At OTH, the reduced form of nitrogen rather than the oxidized form seems to account for the higher N fluxes on this plot (Table IV, Figure 3), probably due to the fact that the OTH forest stand is near to agricultural fields and that ammonia tends to be readily re-deposited locally (e.g. Sutton *et al*., 1998). The concentrations of NO_3^- and NH_4^+ in WD at OTH, VOR and LAU were similar to those measured in 1997–1999 at EMEP stations on the Central Plateau, i.e. 35–45 mg l^{-1} of NO_3^- –N and 40–55 mg l^{-1} of NH_4^+ –N (NABEL, 2000).

NOV and SCH, which had the highest deposition of nitrogen, were on the other end of the deposition range. At NOV, sulfur and proton depositions were also the highest, whereas the S deposition on all the other plots was low to moderate, reflecting the large decrease in SO_2 emissions during the last 15 years. N and S deposition in the open area of NOV was in the upper range of deposition measured at several stations in Southern Switzerland (Barbieri and Pozzi, 2001) and the northern part of Italy bordering Switzerland (Della Lucia *et al*., 1996; Balestrini and Tagliaferri, 2001). The high deposition rates at NOV are related to the high level of emissions from the industrialized and densely populated Po Basin to which the southern part of Switzerland is subjected and the relatively high amount of precipitation compared to the open Po Plain (Della Lucia *et al*., 1996). The Southern Alps have also been recognized as being most sensitive to acid deposition (Rihm, 1994). The high deposition rates at SCH, which clearly exceeded the depositions measured on the two other plots located in the Lower Alps (ALP, BEA), are most likely related to the agricultural activities (livestock farming) carried out in the plain

and to the geographic situation of the plot. It is located on the northern flank of the Alps, where an orographic barrier effect occurs.

4.2. Comparison with modeled deposition

For nitrogen, LWF BP measurements were close to the modeled WD. However, for five plots above 1000 m (BET; ALP, BEA; CEL, NAT), $WD_{N(mod)}$ was higher than $WD_{N(LWF)}$. The difference appears to be related to the modeled N concentrations in precipitation, which were systematically higher than the corrected concentrations measured by LWF. This suggests that the parameters of the linear equation used to model N concentrations above 1000 m should be adjusted. At ALP, the modeled precipitation was moreover noticeably higher than the precipitation amounts measured by LWF over the two sampling years, due to the lower than average precipitation amounts at the site during these two years, which increased the difference between $WD_{N(mod)}$ and $WD_{N(LWF)}$. At plots below 1000 m, the concentrations measured by LWF were scattered around the modeled concentration, assumed to be constant (0.45 mg NH_4^+–N l^{-1}, 0.33 mg NO_3^-–N l^{-1}), but $WD_{N(mod)}$ and $WD_{N(LWF)}$ were in close agreement except at SCH. For the Southern Alps, NH_4^+ and NO_3^- concentrations in wet deposition resulting from the model of Barbieri and Pozzi (2001), which we applied to this part of Switzerland, were both lower than the measured concentrations. However, this might be related to the specific local characteristics of NOV, and possibly CHI as well, rather than to an inaccuracy of the model, which has been calibrated with recent data (1993–1998) from 13 sites in Southern Switzerland (Barbieri and Pozzi, 2001).

In contrast, $DD_{N(mod)}$ was noticeably higher than $DD_{N(LWF)}$ except at NOV. As $DD_{N(LWF)}$ is itself derived from model calculations, it is difficult to determine which of $DD_{N(mod)}$ and $DD_{N(LWF)}$ is closest to the true value for DD_N. In a detailed study of atmospheric deposition in a spruce stand in Alptal close to the ALP LWF plot, DD_N estimated with inferential modeling amounted to approximately 5 kg N ha^{-1} a^{-1} (Fischer-Riedmann, 1995). This value is consistent with $DD_{N(LWF)}$ (4.5 kg N ha^{-1} a^{-1}, Table VI) whereas $DD_{N(mod)}$ (11.1 kg N ha^{-1} a^{-1}) is higher. Measurements of NH_3 and NO_2 on selected LWF plots during 2000 using passive samplers should help to determine the causes of the discrepancies between the modeled and estimated dry deposition values by supplying measured concentrations which can be directly compared to the concentrations used in the resistance model.

It is also worth noticing that the inter-annual variability of LWF deposition measurements was high, especially at NOV, reflecting at least partly the high variability of precipitation. The comparison could yield an entirely different picture if only one sampling year was available. In 1999, when the measured deposition fluxes at NOV were highest ($WD_{N(LWF)} = 28.3$ kg ha^{-1} a^{-1}, $DD_{N(LWF)} = 13.5$ kg ha^{-1} a^{-1}), the modeled values $WD_{N(mod)}$ and $DD_{N(mod)}$ would have been -7.5 and -4.7 kg ha^{-1} a^{-1}, respectively, lower than the LWF values. In contrast, in 1997, when the lowest LWF deposition fluxes were measured, $WD_{N(mod)}$ and $DD_{N(mod)}$ would have

exceeded LWF values by 3.2 and 2.5 kg ha^{-1} a^{-1}, respectively. Besides the precipitation amount, other factors could contribute to the large differences in deposition observed between years, for example, deposition from alkaline dust, transported from the Sahara, occurs occasionally and can result in peaks of base cations in the precipitation samples, which, in turn, influences the output of the canopy budget model.

With regard to sulfur, $WD_{S(LWF)}$ and $WD_{S(mod)}$ were in close agreement, except at NOV, and, to a lesser extent, ALP. In contrast, $DD_{S(mod)}$ tended to be higher than $DD_{S(LWF)}$, even though the model was expected to underestimate sulfur dry deposition since it calculated SO_2 dry deposition only, ignoring particulate sulfate deposition. As a result of elevated $DD_{S(mod)}$, $TD_{S(mod)}$ also tended to be higher than $TD_{S(LWF)}$. $DD_{S(mod)}$ exceeded $DD_{S(LWF)}$, except at NOV, on all the broadleaved plots (NEU, JUS, LAU; OTH; SCH) and at VOR. At VOR, *Abies alba* is the main species, but VOR is actually a mixed stand with a number of broadleaved species. This suggests that, instead of applying a single deposition velocity factor to the modeled SO_2 concentrations regardless of forest type, a distinction should be made between broadleaved and coniferous stands.

4.3. Exceedance of critical loads

Rihm (1996) reported that the critical loads for N in managed forests calculated with the SMB method were exceeded on 95% of the mapped area. Using updated data for the calculation of N deposition (i.e. reference years: 2000 north of the Alps and 1993–2000 south of the Alps instead of 1993–1995 in Rihm's report, and a lower NH_3 deposition velocity for broadleaved stands), the SMB critical loads are still exceeded on 92% of the mapped forest area. The same overall picture is achieved if we compare $TD_{N(mod)}$ to the SMB critical loads on the LWF plots: for all plots, critical loads for N are exceeded. The excess range was greater in Rihm's report than for the LWF plots, however, due to the different years of reference used to model N deposition and the higher deposition velocity applied to NH_3 concentrations in the 1996 report. In addition, the parameter defining the total acceptable N leaching in the equation calculating the critical loads was also modified.

If $TD_{N(LWF)}$ is compared to the SMB critical loads, the overall picture shows more contrasts, with two plots below 1800 m as well as both plots above 1800 m receiving total N deposition lower than the calculated CL_N. When comparing $TD_{N(LWF)}$ with the empirical CL_N, it is even more difficult to make conclusive statements since $TD_{N(LWF)}$ was within the empirical CL_N but not above the upper value of the range for most plots. Only at NOV and SCH did atmospheric deposition of nitrogen exceed both modeled and empirical critical loads.

In addition, when comparing total deposition and calculated CL_N, it must be considered that a substantial margin of error is associated with the critical loads calculated according to the steady state mass balance (SMB CL_N). The denitrification fraction, fde, can only be a very rough estimate of the actual denitrification

rate. Moreover, the degree of hydromorphy derived from the soil suitability map did not always match the degree of hydromorphy indicated by features of oxidation reduction assessed on the soil profiles dug on the plots themselves (Walthert, WSL, personal communication; Walthert *et al*., 2003). The maximum deviation, which can be expected from the "true" value, assuming an acceptable leaching of 4 kg N ha^{-1} a^{-1} and an error on fde of 0.5, is as large as 8 kg N ha^{-1} a^{-1}. The value of U_N (N removal by wood harvesting) is based on regional means, which could be quite different from the actual harvesting rates, so that deviations in the same order of magnitude are to be expected.

4.4. Uncertainties in fluxes

Uncertainties are involved in both the throughfall method and the modeling approach. In the model, one of the main uncertainties probably lies in the deposition velocities. The values of deposition velocities used in the model were either constant or depended on the type of stand (coniferous or broadleaved) or altitude only. We expect that the model results could be improved by taking into account local meteorological and canopy characteristics in the setting of the deposition velocities. Air concentrations of NH_3, NO_2 and SO_2, which were modeled on the basis of the data from 40 to 120 monitoring stations, should be quite reliable. The modeled concentrations of aerosols and concentrations in precipitation, on the other hand, rely on a very limited set of monitoring data. Our measurements of bulk deposition indicate that a better calibration of the model, which calculates concentrations in precipitation, is needed. Since the calculated wet deposition at the plot level is a linear function of concentrations and precipitation amounts, a 50% variation in one of the input parameters would result in a 50% variation in the calculated wet deposition. Likewise, a 50% variation of the deposition velocity would result in a 50% variation of the dry deposition. Since dry deposition of N accounts for 30–70% of the total N deposition, a 50% variation in the deposition velocity would result in a variation of 15–35% in TD_N.

There are a number of uncertainties related to throughfall. The general uncertainties related to the method (e.g. the assumptions of the canopy budget model) should be kept in mind but are not dealt with here (EC-UN/ECE *et al*., 2001). Several uncertainties are specifically related to LWF measurements. Some of them do not lead to systematic under- or overestimation of deposition measurements, including the use in winter of 1–4 snow collectors only on the LWF plots with difficult access in winter, while it is generally known that the spatial variation in throughfall fluxes at the plot scale can be substantial (see Thimonier (1998b) for an analysis of within-stand variability at OTH, and e.g. Houston *et al*. (2002)). Other factors bias estimates of atmospheric deposition in a systematic way, e.g. road salting: NaCl particles blown away by the wind could contaminate bulk precipitation collectors, which would decrease estimations of the dry deposition of base cations and nitrogen in the canopy budget model. Also to be mentioned is a possible contamination

with Na^+ and Ca^{2+} during sample preparation in the laboratory in 1999/2000, as suspected by occasionally higher values in blank samples during this period. Furthermore, since stemflow was not measured, atmospheric deposition was often underestimated, especially on the LWF stands where beech (*Fagus sylvatica* L.) is the main tree species (NEU, LAU, OTH, SCH). In beech stands, stemflow is substantial and can easily account for 10% of incident precipitation (in Thimonier, 1998a). Its contribution to the total deposition can be even higher since it is usually more concentrated than throughfall (Parker, 1983). In a deciduous hardwood forest near Ithaca (NY, USA), Butler and Likens (1995) found that stemflow represents 16% of the S deposition and 12–13% of the N deposition to the forest floor.

A field comparison of 20 different sets of sampling equipment and designs used within ICP Forests showed that precipitation amounts differed by 17.9% on average from measurements obtained with a collocated Hellmann gauge in an open area (Draaijers *et al*., 2001). Precipitation measured by our collectors during this comparison was 13% higher than the precipitation measured by the Hellmann gauge, which led to above average fluxes. This may have been due to the connection between the funnel, bottle and the fine-meshed filter used before March 2001 not being tight. Yet, the bulk precipitation amounts measured by LWF at ALP were in close agreement (0.9% lower in 1997 and 2.7% lower 1998) with those measured using a heated tipping bucket of a collocated WSL weather station which is set according to WMO standards (Stähli, WSL, personal communication; description of installation see e.g. Keller *et al*. (1989); Burch *et al*. (1996)). Inorganic nitrogen fluxes in BP were 13.6 kg N ha^{-1} for the hydrology project (Stähli, WSL, personal communication) and 13.9 kg N ha^{-1} for LWF. Other sampling equipment used in the NITREX project (see e.g. Schleppi *et al*., 1998) in a nearby area measured similar precipitation amounts to those in LWF, but recorded approximately 2 kg N ha^{-1} less nitrogen than LWF (Schleppi, WSL, personal communication). However, S fluxes measured in the NITREX and LWF projects were similar. It is possible that the observed differences in N fluxes could be ascribed to the different exposure of the open areas to local emissions of nitrogen, since the open areas of the NITREX and LWF projects are 250 m apart. At ALP, rain collectors were in use for part of the year only, but overall the comparison results suggest that the filter did not greatly influence our assessments of annual fluxes.

A further source of uncertainty is that the chemical composition of the samples over the two-week collection period may change, especially in summer. Nitrogen compounds are especially unstable (see e.g. literature review by Thimonier, 1998a), so we have not discussed in detail the relative contributions of NO_3^- and NH_4^+ to the total dissolved inorganic N deposition at the LWF plots. A decrease in NH_4^+ concentrations over time has been frequently reported (Liechty and Mroz, 1991; Ferm, 1993). This may be due to micro-organisms transforming NH_4^+ into organic forms or to nitrification. We have only presented the concentrations and fluxes of inorganic nitrogen. The inclusion of the dissolved organic fraction would yield higher nitrogen fluxes. In 2001, most of the samples were analyzed with the

combustion method, and for a rough estimate, we corrected the total dissolved nitrogen concentrations for those few samples having been analyzed with the alkaline persulfate oxidation method. The flux of DON in throughfall was then between 0.8 and 4.2 kg N ha^{-1} (lowest fluxes in CEL, highest fluxes in VOR), which represented 10.7% (OTH) to 26.1% (VOR) of the total dissolved nitrogen flux under the canopy. In the open area, DON fluxes in BP were usually <1 kg N ha^{-1} (OTH: 1.2 kg ha^{-1}). Before 2001, the corrected DON fluxes were much higher both in BP (on average 3.1 kg N ha^{-1} a^{-1}, with a maximum of 7.4 kg ha^{-1} in OTH in 1996) and in TF (up to 11.6 kg N ha^{-1} in 1999 in LAU, which represented 39.7% of total dissolved nitrogen). Therefore, if dissolved organic N is included in the total N deposition, some of the plots for which the inorganic N deposition is within the critical loads range (Table VII) would be ranked among the plots where critical loads are exceeded.

5. Conclusion

In this comparison of modeled and measured atmospheric deposition on 13 LWF plots, we found that the wet deposition of N and S derived from bulk deposition measurements were close to the modeled values, whereas estimates of the dry deposition of both N and S with the throughfall method using the canopy budget model were generally lower than the modeled values. In this comparison exercise, the high year-to-year variability of deposition shown by our measurements should be kept in mind. This high inter-annual variability stresses the need of having long enough measuring periods to assess atmospheric deposition on a site.

As regards wet deposition, the few differences observed between $WD_{N(mod)}$ and $WD_{N(LWF)}$ suggest that the linear model used to calculate N concentrations in precipitation above 1000 m should be improved. However, modeled and measured values were in agreement on the whole.

The difference between LWF estimates and modeled values of dry deposition is probably partly due to the deposition velocities and the air concentrations used in the model. Passive sampling of NH_3 and NO_2 on selected LWF plots during 2000 (analysis in process) will make it possible to check the relevance of the air concentrations used in the model. The values of deposition velocities could be adjusted more finely by including information on turbulence in the boundary layer of the atmosphere (e.g. wind speed, surface roughness of topology and vegetation), as well as information on factors influencing the surface resistance (e.g. humidity).

The results of the throughfall method could also be improved. Especially for beech stands, stemflow measurements should be included when measuring throughfall. The actual contribution of stemflow to deposition fluxes will soon be assessed at OTH and LAU, where stemflow is currently being sampled. Further improvements could be achieved by quantifying specifically for each site the correction

factors used to derive wet deposition from bulk deposition by running wet-only deposition collectors and bulk collectors in parallel for a limited time period. The weak acids should be better quantified, and the assumptions of the canopy budget model also need to be experimentally tested for our site conditions. In particular, the relative exchange efficiencies of H^+, NO_3^- and NH_4^+ should be determined for the main tree species on the plots. In addition, alternative approaches should also be explored to estimate the dry deposition of N, which is the component with the most uncertainties involved (e.g. micrometeorological methods, which include eddy correlation and gradient techniques, but which are technologically complex and expensive; wash studies using natural or artificial leaves as collectors).

In spite of the discrepancies between measured and modeled values, both methods resulted in total deposition estimates of N which exceeded the calculated critical loads for N and which were within or above the range of empirical critical loads for most of the plots. The two plots located above 1800 m were, however, exceptions (CEL, NAT). On the plots where critical loads are exceeded, ecological changes are expected to occur or may already be underway. Tree growth may be stimulated at some plots, but negative changes, such as a decrease in the species diversity of the ground vegetation, nutrient imbalances, or nitrate leaching could also take place. LWF will continue to study the various compartments of the ecosystems at the LWF plots to detect possible dysfunction or imbalances.

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